U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-271 008

High-Temperature Desulfurization of Low-Btu-Gas

Consolidation Coal Co, Library, Pa Research Div

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

Apr 77

PB 271 008

EPA

EPA-600/7-77-081
April 1977

HIGH-TEMPERATURE DESULFURIZATION OF LOW BTU GAS

Interagency
Energy-Environment
Research and Development
Program Report

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
[illegible]

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into seven series. These seven broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The seven series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-77-031
2.
3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE High-Temperature Desulfurization of Low-Btu Gas
5. REPORT DATE April 1977
6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) G. P. Curran, B.J. Koch, B. Pasek, M. Pell, and E. Gorin
8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS
Consolidation Coal Company
Library, Pennsylvania 15129
10. PROGRAM ELEMENT NO. EHB529
11. CONTRACT/GRANT NO. 68-02-1333
12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711
13. TYPE OF REPORT AND PERIOD COVERED Final; 7/73-1/76
14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES EPA project officer for this report is S.L. Rakes, Mail Drop 61, 919/549-8411 Ext 2825.

16. ABSTRACT

The report describes and gives results of economic studies of a process for desulfurizing low-Btu fuel gas. The gas is first desulfurized at high temperature in a fluidized bed of half-calcined dolomite. It is then cooled to 700 C and passed through high-pressure-drop cyclones to remove particulates and alkali. The gas is intended for use as fuel to gas turbines in combined-cycle power generation. The sulfur acceptor is regenerated with steam and CO_2. A liquid-phase Claus reactor is used to process H_2S in the regenerator offgas into elemental sulfur. Experimental data are presented in several areas: desulfurization and regeneration activity of dolomites as a function of cycles; batch studies to determine variable effects and rate data; particulate and alkali removal at high temperature; Chance reaction studies; and process improvement studies. Two economic studies were performed: one showed an incentive accruing to the process versus a conventional wet desulfurization scheme; and the other, an update of the process economics, showed that a plant designed in 1975 for 1980 operation would desulfurize gas from a high-sulfur coal for 38 ¢/MM Btu (HHV + sensible heat) delivered to a power station.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Fluidizing	Air Pollution Control	13B	13H
Coal Gas	Dolomite	Stationary Sources	21D	08G
Manufactured Gas	Fines	Low-Btu Gas		
Desulfurization	Alkalies	Particulate	07A, 07D	
Regeneration (Engineering)		Chance Process		
		Claus Reactor		
		Fuel Gas		

18. DISTRIBUTION STATEMENT Unlimited
19. SECURITY CLASS (This Report) Unclassified
21. NO. OF PAGES 361
20. SECURITY CLASS (This page) Unclassified
22. PRICE A16-A01

EPA Form 2220-1 (9-73)

EPA-600/7-77-031
April 1977

HIGH-TEMPERATURE DESULFURIZATION OF LOW-BTU GAS

by

G.P. Curran, E.J. Koch, B. Pasek,
M. Pell, and E. Gorin

Consolidation Coal Company
Library, Pennsylvania 15129

Contract No. 68-02-1333
Program Element No. EHB529

EPA Project Officer: S.L. Rakes

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, N.C. 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

ABSTRACT

A process for the desulfurization of low-Btu fuel gas is described. Processing consists of first desulfurizing the gas at high temperature in a fluidized bed of half-calcined dolomite. The gas is then cooled to 760°C and passed through high-pressure drop cyclones to remove particulates and alkali. The intended end use of the gas is as fuel to gas turbines in combined cycle power generation. The sulfur acceptor is regenerated with steam and CO_2. A liquid-phase Claus reactor is used to process H_2S in the regenerator offgas into elemental sulfur.

Experimental data are presented in the following areas:

1. Desulfurization and regeneration activity of Canaan, Tymochtee and Buchanan dolomites as a function of cycles. The Buchanan and Tymochtee stones were subjected to various degrees of hardening.
2. Batch studies to elucidate variable effects and rate data.
3. Removal of particulates and alkali at elevated temperature.
4. Chance reaction studies. The Chance reaction is a low temperature wet process for desulfurizing spent stone and rendering it suitable for disposal.
5. Process improvement studies.

Two economic studies of the process were done. The first showed an incentive accruing to the process vis-a-vis a conventional wet desulfurization scheme. The second was an update of the process economics which showed that a plant designed in 1975 for 1980 operation would desulfurize gas from a high-sulfur coal for 38¢/MM Btu (HHV + sensible heat) delivered to a power station.

This report was submitted by Consolidation Coal Company (also known as Conoco Coal Development Company) in partial fulfillment of Contract No. 68-02-1333 under sponsorship of the Advanced Process Branch of the Energy Assessment and Control Division, Industrial Environmental Research Laboratory of the Environmental Protection Agency. The work was done during the period July, 1973 to January, 1976.

TABLE OF CONTENTS

Page

I. SUMMARY 1
II. CONCLUSIONS AND RECOMMENDATIONS 7
III. ECONOMIC EVALUATION 11

A. Introduction 11
B. Summary 11

Table III-1 - Summarized Economic Evaluation - Regenerative Acceptor Desulfurization Process 12
Figure III-1 - Simplified Schematic of Expander Turbine plus Conventional Boiler and Steam Cycle 14

C. Process Description 15

Figure III-2 - Block Flow Diagram - Overall System 16
Figure III-3 - Process Flow Diagram, Low-Sulfur Boiler Fuel Regenerative Acceptor Case, Dwg. AF-3667 17

D. Design Basis 19

Table III-2 - Mass and Heat Balance - Gas Desulfurizer 23

E. Material and Heat Balances 24
F. Plant Investment and Operating Cost Estimates 24

Table III-3 - Mass and Heat Balance - Acceptor Regenerator 25
Table III-4 - Mass and Heat Balance - Acceptor Stripping Column 26
Table III-5 - Mass and Heat Balance - Liquid-Phase Claus Reactor 27
Table III-6 - Mass and Heat Balance - Sulfur Combustor 28
Table III-7 - Mass and Heat Balance - SO_2 Absorption Tower 29
Table III-8 - Overall Mass and Heat Balance 30

G. Evaluation of System Economics 32

Table III-9 - Investment Summary 33
Table III-10 - Direct Operating Cost Summary Ex. Acceptor Cost 34
Table III-11 - Economic Evaluation - Regenerative Acceptor Desulfurization Process 35
Figure III-4 - Sensitivity Analysis 37

H. Artificially Hardened Sorbents 38

Figure III-5 - Potential Impact of Combined Cycle Power Station Efficiencies on Desulfurization Economics 39
Figure III-6 - Hardening Process 40
Table III-12 - Mass and Heat Balance - Hardening Desulfurizer 41
Table III-13 - Producer Gas Compositions with and without Hardening 42

J. Technical Uncertainties 42

TABLE OF CONTENTS - Cont'd.

Page

IV. EQUIPMENT AND PROCEDURE 44

A. Gas Desulfurizer-Regenerator System 44
B. Hardness Testing 45
C. Fine $CaCO_3$ Runs 45

Figure IV-1 - P&I Flow Diagram, Continuous Unit, Acceptor Reaction Loop, Dwg. AF-3411 46
Figure IV-2 - CS_2 Supply System 47
Figure IV-3 - Drop Tester for Acceptor Hardness - Dwg. DM-3461 48

D. Hot Removal of Particulates and Alkali Fume 49

Figure IV-4 - Flow Diagram for Desulfurization by Chalk Slurry 50
Figure IV-5 - Flow Diagram for Desulfurization by Fine Limestone and/or Chalk 51
Figure IV-6 - Flow Diagram for Ash and Alkali Fume Removal Study 52
Figure IV-7 - Filter for Alkali Fume Removal System, Dwg. DV-3592 53
Figure IV-8 - Heating Chamber - Alkali Fume Removal System with Filter Clean-up Assembly, Dwg. AV-3586 55

E. Chance Reaction 56
F. Lab-Scale Batch Acceptor Cycling Reactor 57

Figure IV-9 - Reactor Assembly - Lab-Scale Acceptor Cycling Reactor, Dwg. AV-3627 58

G. Reduction of $CaSO_4$ by H_2S 59

Figure IV-10 - Flow Diagram - Batch Acceptor Cycling Reactor, Dwg. CF-3446 60
Figure IV-11 - Sulfur Condensing System No. 1 61
Figure IV-12 - Sulfur Condensing System No. 2 62

V. MATERIALS: SOURCE, PREPARATION AND ASSAYS 63

A. Sulfur Acceptors 63
B. Acceptor Assays 63

Table V-1 - Results of Raw Stone Assays 64

C. Low-Temperature Ash 65

Table V-2 - Elemental Analyses of Dolomites 66
Table V-3 - Ash from Illinois No. 6 Coal 65
Figure V-1 - Preparation of Low-Temperature Ash 67
Table V-4 - Coal Based Materials for Alkali Fume Removal Study 68
Table V-5 - Analyses of Dolomite Feeds to Alkali Fume Removal Study 70

TABLE OF CONTENTS - Cont'd.

Page

VI. SAMPLE CALCULATIONS 71

A. Calculation of Required Make-Up Rate 71

Table VI-1 - Computer Program for Cycling Acceptor 72
Table VI-2 - Computer Output for Canaan Dolomite 74
Figure VI-1 - Equilibrium $CaCO_3$ in Canaan Dolomite as a Function of Conversion and Make-up Rate 75
Figure VI-2 - Equilibrium $CaCO_3$ in Hardened Tymochtee 9 Dolomite as a Function of Conversion and Make-up Rate 76

B. Calculation of Normalized Density 77

Figure VI-3 - Equilibrium $CaCO_3$ in Hardened Buchanan Dolomite as a Function of Conversion and Make-up Rate 78

VII. TABULAR CHRONOLOGICAL HISTORY OF RUNS 79

Table VII-1 - Summary of Initial Runs with Canaan Dolomite 80
Table VII-2 - Summary of Early Hardening Runs 81
Table VII-3 - Summary of Runs with Sorbent from Various Hardening Conditions 82
Table VII-4 - Summary of Chance Product Runs 84
Table VII-5 - Summary of Main Body of Continuous Runs 85
Table VII-6 - Batch Studies of Process Variables 90
Table VII-7 - $CaSO_4$ Reduction by CaS 95
Table VII-8 - Low Temperature Ashing of Coal 96
Table VII-9 - Alkali Fume Removal 97

VIII. CYCLIC CONTINUOUS RUNS WITH CANAAN DOLOMITE 99

A. Introduction 99
B. Runs without Makeup 99

Table VIII-1 - Conditions and Results for Gas Desulfurizer with Canaan Dolomite Feed 100
Table VIII-2 - Conditions and Results for Regenerator with Canaan Dolomite Feed 101
Figure VIII-1 - Run A20A - Mol % CaS in Exit Solids 102
Figure VIII-2 - Deactivation of CaS in Canaan Dolomite at 704°C (1300°F) 104
Figure VIII-3 - Run A21 - Mol % CaS in Exit Solids 106
Figure VIII-4 - Run A22A - Mol % CaS in Exit Solids 107
Figure VIII-5 - Deactivation of CaS with Temperature as a Parameter 108
Figure VIII-6 - Run A36A - Mol % CaS in Exit Solids 109
Figure VIII-7 - Run A48 - Mol % CaS in Exit Solids 110

C. Runs with Makeup 113

Figure VIII-9 - Run A51 - Mol % CaS in Exit Solids 114

TABLE OF CONTENTS - Cont'd.

		Page
	Figure VIII-10 - Three Possible Correlations for Deactivation of CaS in Canaan Dolomite at 704°C (1300°F)	115
	Figure VIII-11 - Run A51 - Mol % CaS in Regenerator Exit	116
D.	Density Measurements on Cycled Canaan Dolomite	117
	Figure VIII-12 - Run A52A - Mol % CaS in Exit Solids	118
	Figure VIII-13 - Run A52A - Predicted CaS Contents for Several Correlations	119
	Figure VIII-14 - Run A52A - Mol % CaS in Regenerator Exit	120
	Table VIII-3 - Density of Sulfided Canaan Dolomite	121
	Figure VIII-15 - Normalized Density of Sulfided Canaan Dolomite	122
E.	Attrition Data	123
F.	Conclusions	123
	Figure VIII-16 - Normalized Density of Sulfided Canaan Dolomite from Makeup Runs	124
	Figure VIII-17 - Attrition Data for Canaan Dolomite	125
	Figure VIII-18 - Attrition Data for Runs with Makeup	126
IX.	CYCLIC CONTINUOUS RUNS WITH HARDENED DOLOMITES	129
A.	Introduction	129
B.	Batch Hardening Tests	129
	Table IX-1 - Conditions for Batchwise Dolomite Sulfiding	130
	Table IX-2 - Conditions for Batchwise Oxidation of Sulfided Dolomite	130
	Table IX-3 - Properties of Materials from Hardening Study	131
	Table IX-4 - Results of Drop Tests	134
	Table IX-5 - Conditions and Results for Gas Desulfurizer with Tymochtee Dolomite	136
C.	Continuously Hardened Tymochtee 10 Dolomite	137
	Table IX-6 - Conditions and Results for Regenerator with Tymochtee Dolomite	138
	Figure IX-1 - Run A23 - Mol % CaS in Exit Solids	139
	Figure IX-2 - Run A23 - Deactivation of CaS at 704°C (1300°F)	140
	Table IX-7 - Conditions for Continuous Sulfidation of Tymochtee Dolomite	142
	Table IX-8 - Conditions for Continuous Oxidation of Sulfided Tymochtee Dolomite	143
	Figure IX-3 - Run A24 - Mol % CaS in Exit Solids	144
	Figure IX-4 - Run A24 - Deactivation of CaS at 704°C (1300°F)	145
	Figure IX-5 - Run A25 - Mol % CaS in Exit Solids	146
	Figure IX-6 - Deactivation of Hardened Tymochtee 10 Dolomite at 704°C (1300°F)	148
	Figure IX-7 - Run A26 - Mol % CaS in Exit Solids	149
	Figure IX-8 - Run A27 - Mol % CaS in Exit Solids	150

TABLE OF CONTENTS - Cont'd.

Page

Figure IX-9 - Run A28 - Mol % CaS in Exit Solids 151
Figure IX-10 - Run A29 - Mol % CaS in Exit Solids 151
Figure IX-11 - Deactivation of Tymochtee 10 Dolomite at 704°C (1300°F) 152
Figure IX-12 - Run A30 - Mol % CaS in Exit Solids 154

D. Tymochtee No. 9 Dolomite 155

Figure IX-13 - Run A32 - Mol % CaS in Exit Solids 156
Figure IX-14 - Deactivation of CaS in Hardened Tymochtee 9 Dolomite at 704°C (1300°F) 157
Table IX-9 - Particle Size Consist of Overhead Fines 158

E. Tymochtee No. 11 Dolomite 159

Figure IX-15 - Run A35 - Mol % CaS in Exit Solids 160
Figure IX-16 - Run A37 - Mol % CaS in Exit Solids 161
Figure IX-17 - Deactivation of Tymochtee 11 Dolomite at 704°C (1300°F) 162
Figure IX-18 - Run A38 - Mol % CaS in Exit Solids 163
Figure IX-19 - Run A42 - Mol % CaS in Exit Solids 164

F. Buchanan Dolomite 165

Figure IX-20 - Run A45 - Mol % CaS in Exit Solids 166
Figure IX-21 - Run A46 - Mol % CaS in Exit Solids 167
Table IX-10 - Conditions for Continuous Sulfidation of Buchanan Dolomite 168
Table IX-11 - Conditions for Continuous Oxidation of Sulfided Buchanan Dolomite 168
Table IX-12 - Conditions and Results for Gas Desulfurizer with Buchanan Dolomite 169
Table IX-13 - Conditions and Results for Regenerator with Buchanan Dolomite 170
Figure IX-22 - Deactivation of CaS in Hardened Buchanan Dolomite at 704°C (1300°F) 171
Figure IX-23 - Run A33 - Mol % CaS in Exit Solids 172

G. Density of Buchanan Dolomite 173

Figure IX-24 - Run A63 - Mol % CaS in Exit Solids 174
Figure IX-25 - Run A64A - Mol % CaS in Exit Solids 175
Figure IX-26 - Run A67 - Mol % CaS in Exit Solids 176
Figure IX-27 - Normalized Density of Hardened Buchanan Dolomite 177
Table IX-14 - Density of Hardened Buchanan Dolomite 178

H. Conclusions

X. BATCH SULFIDATION AND REGENERATION EXPERIMENTS 181

A. Batch Sulfidation Studies 181

TABLE OF CONTENTS - Cont'd.

Page

Table X-1 - Conditions for Batch Sulfidation Runs 182
Table X-2 - Properties of Feeds and Products 183
Table X-3 - Results of Sulfidation Runs 184
Table X-4 - Mols H_2S Fed/Hr Per Mol $CaCO_3$ Remaining at 0.10% H_2S in Exit Gas 185
Table X-5 - ANOVA for Mols H_2S/Hr-Mol $CaCO_3$ at Breakthrough 186
Table X-6 - Mol % H_2S in Dry Outlet Gas with Excess $CaCO_3$ Remaining in the Bed 187
Table X-7 - ANOVA for Mol % H_2S in Dry Outlet Gas 188

B. Batch Regeneration Study 189

Table X-8 - Typical Conditions for Batch Regeneration Runs 190

C. Regeneration Kinetics 191

Table X-9 - Results of Regeneration Runs 192
Table X-10 - Regeneration Results - Percent Regeneration 193
Table X-11 - ANOVA for Percent Regeneration 193
Figure X-1 - Approach to Equilibrium vs CaS: Reactants Ratio 194
Figure X-2 - Regeneration of CaS at 649°C (1200°F) 195
Figure X-3 - Regeneration of CaS at 704°C (1300°F) 196
Figure X-4 - Regeneration of CaS at 760°C (1400°F) 197
Figure X-5 - Regeneration of CaS at 816 and 871°C 198

D. Cyclic Sulfidation and Regeneration 199

Table X-12 - Initial Rate Constants for Regeneration Kinetics 200
Figure X-6 - Effect of Temperature on Regeneration Kinetics 201
Table X-13 - History and Cycling Results for Reactivated Dolomite 202
Table X-14 - Conditions and Results for Gas Desulfurizer 204
Table X-15 - Conditions and Results for Regenerator 205
Table X-16 - Run A86 - Batch Cycling of Run A22A Dolomite 206

E. Cycling with Varying Residence Times 207
F. Lab-Scale Batch Acceptor Cycling 207

Figure X-7 - Run A128 Deactivation of CaS at 704°C (1300°F) 208
Table X-17 - Conditions and Results for Gas Desulfurizer Runs A129 to A132 209
Table X-18 - Runs A129 to A132 - Conditions and Results for Regenerator 210
Figure X-8 - Runs A129, A129A - Deactivation of CaS at 704°C (1300°F) 211
Figure X-9 - Runs A130 to A132 - Deactivation of CaS at 704°C (1300°F) 212
Table X-19 - Conditions for Batch Acceptor Cycling Reactor 214
Table X-20 - Results of Lab-Scale Cycle Test CR1 215
Figure X-10 - Lab-Scale Batch Acceptor Cycling 216
Table X-21 - Results of Lab-Scale Cycle Test CR2 217
Table X-22 - Screen Analysis of Run CR2 After 22 Cycles 218

TABLE OF CONTENTS - Cont'd.

Page

XI. HOT REMOVAL OF PARTICULATES AND ALKALI 219

Table XI-1 - Conditions and Results for Gas Desulfurizer 220
Table XI-2 - Conditions and Results for Regenerator 221
Table XI-3 - Material Balances - Alkali Fume Removal Runs 222
Table XI-4 - Molar Ratios in Effluent Downstream of Hot Box Filter 224

XII. CHANCE REACTION STUDIES 225

A. Introduction 225
B. Discussion 225

Table XII-1 - Conditions and Results for Sulfidation of Chance Reaction Products 226
Table XII-2 - Chance Reaction: Conditions and Results 228

C. Conclusions 229

Table XII-3 - Chance Reaction: Composition of Slurry and Exit Gas 230

XIII. PROCESS IMPROVEMENT STUDIES 231

A. Introduction 231
B. Use of Fine Calcined Limestone 231

Table XIII-1 - Conditions and Results for Fine CaCO$_3$ Runs 232

C. Generation of an Active Acceptor from Coarse Limestone 233
D. Fully Calcined Dolomite 233

Table XIII-2 - Particle Size Analysis of Product Limestone Fines 234
Table XIII-3 - Analysis of Product Limestone Fines 234
Figure XIII-1 - Run A41 - Deactivation of CaS at 704°C (1300°F) 235
Table XIII-4 - Conditions and Results for Gas Desulfurizer 236
Table XIII-5 - Conditions and Results for Regenerator 237
Table XIII-6 - Results of Sulfidation Runs with Fully Calcined Dolomite 238

E. Reaction of CaSO$_4$ with H$_2$S to Product Liquid Claus Feed 239

Figure XIII-2 - Run A123 Deactivation of CaS at 704°C (1300°F) 240
Figure XIII-3 - Modified Sulfur Recovery Section 242
Table XIII-7 - Conditions and Results for Reaction of CaSO$_4$ with H$_2$S 243
Table XIII-8 - Acceptor Compositions for Runs A84C and A84D 244

F. Conclusions 245

Table XIII-9 - Calculated Gas Compositions, Run A84 246
Table XIII-10 - Comparison of Dry Gas Compositions, Run A84 247

TABLE OF CONTENTS - Cont'd.

		Page
XIV.	PHYSICAL EXAMINATION OF PRODUCT SOLIDS	249
	A. Surface Area and Pore Volume Data	249
	B. Sulfur Distribution in Sulfided Dolomites	249
	Table XIV-1 - Surface Area and Pore Volume Data	250
	C. Scanning Electron Microscope Examinations	251
	Figure XIV-1 - Images of Sample A61-1 at 180X - Prerun Sulfided to 15 mol % CaS	253
	Figure XIV-2 - Images of Sample A62-1A at 200X - Prerun Sulfided to 15 mol % CaS	254
	Figure XIV-3 - Images of Sample A62-2 at 180X - Prerun Oxidized to 14 mol % $CaSO_4$	255
	Figure XIV-4 - Images of Sample A62-2A at 150X - Prerun Oxidized to 14 mol % $CaSO_4$	256
	Figure XIV-5 - Images of Sample A62-3 at 150X - Regenerator Sample, 0.7 cycles, 25 mol % CaS	257
	Figure XIV-6 - Images of Sample A62-3A at 150X - Regenerator Sample, 0.7 cycles, 25 mol % CaS	258
	Figure XIV-7 - Images of Sample A62-4 at 150X - Regenerator Sample, 9.6 cycles, 72 mol % CaS	259
	Figure XIV-8 - SEM Photos of A78 Product	260
	Figure XIV-9 - SEM Photos of A81 Feed and Product	261
	Figure XIV-10 - SEM Photos of A66 Desulfurizer Bed	262
	Figure XIV-11 - SEM Photos of A66 Desulfurizer Bed	263
	Figure XIV-12 - SEM Photos of A66 Desulfurizer Bed	264
XV.	SUMMARY OF VARIABLE EFFECTS	265
	A. Gas Desulfurizer	265
	B. Regenerator	266
	C. Model for the Deactivation Process	266
XVI.	DESIGN BASIS	269
	A. Gas Desulfurizer	269
	Table XVI-1 - $H_2S:CaCO_3$ Ratio for Continuous Runs	270
	B. Regenerator	271
	C. Tertiary Particulate Removal	271
	Table XVI-2 - Stone Make-up Summary	272
XVII.	ENVIRONMENTAL EVALUATION	273
	Table XVII-1 - Trace Elements in 90 Illinois Limestone Samples	273
	Figure XVII-1 - Process Flow Schematic - Materials Consumed and Generated (TPY)	274
	Table XVII-2 - Phosphorous Pentoxide, Manganese Oxide, and Sulfur Trioxide in Illinois Limestone and Dolomites Containing more than 95% Carbonates	275

TABLE OF CONTENTS - Cont'd.

PAGE

XVIII. REFERENCES 279

XIX. APPENDICES

Appendix A - Detailed Investment Cost 283

Table A-1 - Cost Estimate: Section 300, Sulfur Removal 284
Table A-2 - Cost Estimate: Section 400, Sulfur Removal 286

Appendix B - Data Tables 287

Table B-1 - Composition of Exit Solids from Cycling Runs 288
Table B-2 - H_2S Content of Exit Gas from Cycling Runs 293
Table B-3 - Attrition Data 298
Table B-4 - H_2S Content of Exit Gas - Batch Variable Studies 301

Appendix C - Thermodynamic Data 305

Table C-1 - Effect of Temperature and Sulfur Partial Pressure on Distribution of Sulfur Species 307
Table C-2 - Equilibrium Constants for Gas Reactions 308
Table C-3 - Numerical Values of Equilibrium Constants for Table C-2 309
Table C-4 - Heat Capacities at Zero Pressure 310
Table C-5 - Mean Heat Capacities Above 60°F, Gases 311
Table C-6 - Heats of Formation at 25°C, Gases 312
Table C-7 - Equilibrium Constants for Solids Reactions 313
Table C-8 - Mean Heat Capacities Above 60°F, Solids 314
Table C-9 - Heats of Formation at 25°C, Solids 315
Figure C-1 - Sulfur Vapor Pressure 316
Figure C-2 - Equilibria for CaS Reactions 317
Figure C-3 - Equilibria for CaS Reactions 318

Appendix D - Comparison of CGDC Process to Hot Carbonate Scrubbing 319

Memorandum RR-13451 - Cost of Pressurized Producer Gas Desulfurization 320

Appendix E - Conversion Factors - English to Metric Units 349

I. SUMMARY

A. Process Description and Economic Evaluation

The process evaluated here is an evolution of the dolomite-based hot clean-up process described in the last annual report.(1) The economic study was limited to a consideration of the hot gas cleanup with exclusion of the gasification process. A process flow diagram along with summarized heat and material balances, operating conditions, etc., are given in Figure III-8. The basis for the study was supplying hot clean producer gas to a boiler capable of producing 1400 MW of electric power.

The study included in the last annual report(1) was modified to take into account the effect of inflation for a new presumed start up date of January 1980. Further modifications were made in the process design assumptions to take into account the results of the last two years of experimental work. A brief economic comparison of the updated previous design and the present design is given below. Capital charges are at the rate of 18% of the investment and the operating factor is assumed to be 70%.

	Present Design	Updated Previous Design
Capital Cost, $/KW	58	53.4
Gas Desulfurization Cost, ¢/MM Btu (HHV + Sensible Heat)	36	32.5

B. Continuous Bench-Scale Studies

1. Cycling Studies - Canaan Dolomite

The cycling of Canaan dolomite in the continuous bench-scale unit was further studied through the gas desulfurization and regeneration units.

The principal extension of previous work was the use of longer runs to increase the number of cycles, the study of the effect of acceptor particle size, the investigation of the effect of higher temperature and higher H_2S concentrations on regeneration rate, and the study of cycling with continuous addition of fresh stone to supplement previous batch cycling studies.

The major result of this program was to demonstrate that Canaan dolomite showed acceptable life and activity. Hydrogen sulfide was removed in the gas desulfurization step to closely approach equilibrium even with very low inventory levels of $CaCO_3$. A high hydrogen sulfide concentration in the regenerator does not affect the rate of regeneration and close approach to equilibrium is obtained. Regeneration rates are improved by an increase in regeneration temperature.

The runs with continuous acceptor makeup showed results consistent with the correlation for acceptor activity versus cycles developed from batch data. Acceptor make-up rates can thus be closely estimated from the "batch" cycling runs.

Increase of particle size had no effect on acceptor activity, but its effect on attrition rate was difficult to assess.

Attrition rates in the cycling runs were uniformly low, i.e., generally less than one percent.

2. Hardening and Cycling Studies - Other Dolomites

A number of dolomites do not show sufficient attrition resistance for direct use in the process. A process was developed for hardening of "soft" dolomites.

The hardening process was first developed batchwise and then applied in continuous equipment. The hardening process consisted of first partially sulfiding the stone and then oxidizing the sulfided stone to calcium sulfate. The oxidized stone is fed directly to the gas desulfurizer where the calcium sulfate is reduced "in situ" to calcium sulfide. All three reactions can be conducted in the temperature range of the gas desulfurizer, i.e., at 1600-1700°F. The hardening process is thought to be due to the formation of transient liquids in the $CaS-CaCO_3-CaSO_4$ system.

The commercial process would carry out the process directly in the gas desulfurizer by injection of the "hardening" oxidizing air into a draft tube. Demonstration of this "simplified" version of the process requires pilot plant demonstration.

The process was successfully applied to two "soft" dolomites, i.e., three different batches of Tymochtee dolomites from Ohio and Buchanan dolomite from Virginia.

The attrition rate of the hardened stones in the 35 x 48 mesh size range was reduced to below the targeted value of one percent per cycle. Attrition rate decreased on continued cycling. The effect of particle size on attrition rate was hard to establish due to experimental difficulties.

The hardening process is associated with some loss of acceptor regeneration activity in the cycling process. The activity of the hardened stone was also shown to be independent of particle size over the range tested, i.e., 20 x 28, 28 x 35 and 35 x 48 mesh.

The loss of activity increases with severity of conditions in the hardening step.

The activity of the hardened stones was similar to the Canaan standard, and varied between being slightly poorer to slightly better than the standard depending on the specific batch of stone and hardening conditions employed.

C. Batch Kinetic and Cycling Studies

The above studies were conducted to extend the range of variables and to aid in developing a kinetic model of the process. The work was not carried forward far enough to develop a comprehensive kinetic model. It was shown, however, that the regeneration process may be characterized as a "pseudo" first order process.

The major effects of the variables in the regenerator and desulfurizer were similar to those noted in the continuous unit.

The space velocity in the gas desulfurizer defined as mols H_2S fed/hr-mol $CaCO_3$ inventory at the point of incipient H_2S breakthrough was found to be statistically independent of the following variables:

$CaCO_3$ age
Type of stone but limestones inactive
Bed depth
Particle size
Mol % H_2S in the inert gas

However, space velocity increased with increasing temperature.

The regenerator performance in the batch runs was characterized by the percent regeneration of the CaS. The percent regeneration decreased with increased stone age, and increased with increasing temperature and bed depth. It was also adversely affected by prehardening of the stone. An important finding is the acceleration of the regeneration reaction by H_2S in the product gas.

Cycling studies showed the following important results. The rate of deactivation under similar conditions was approximately the same as in the continuous unit. High temperature regeneration is not useful, however, as a reactivation method since a large portion of the $CaCO_3$ produced is inactive in the gas desulfurizer.

The most significant finding of the batch cycling work is the marked effect of reduced residence time in the gas desulfurizer in improving the regeneration performance and cycle life.

D. Chance Reaction Studies

The major variables of particle size, temperature, acceptor type, stirrer speed and CO_2 flow rate were studied. Runs also were made to simulate two stage as well as countercurrent operation as visualized in the commercial process.

Increasing temperature, CO_2 flow rate and decreasing particle size increased reaction rate. The other variables had a relatively minor effect. The use of two stage or countercurrent operation appears advantageous. Substantially complete sulfur rejection is obtained at atmospheric pressure, 90°C, and one hour residence time.

E. Liquid-Phase Claus Studies

No further experimental work was performed since the last annual report.(1)

F. Properties of Product Solids

Studies were made on the properties of the product acceptor solids to shed light on the mechanism of deactivation. These studies included measurements of particle density, surface area, pore volume, scanning electron microscopic studies (SEM) and distribution of sulfur, calcium and magnesium in the acceptor particles via X-ray and ultraviolet techniques.

The results of these studies although by no means complete are consistent with the following hypothesis for the mechanism of deactivation.

Deactivation occurs mainly in the gas desulfurizer. Crystal growth of $CaSO_4$ and CaS, but primarily the latter segregates the calcium crystals from the MgO. The large CaS crystals in particular are relatively inactive in regeneration and gradually accumulate on cycling.

G. Hot Removal of Particulates and Alkali

Preliminary experimental work was conducted to evaluate in an exploratory way the "substantially" complete hot removal of alkali fume and particulate material.

The preferred device, i.e., high pressure drop cyclones, could not be evaluated due to the small scale of the equipment and limited time available for the work. A hot porous stainless steel filter operated at 1300°F (704°C) was used in this work.

The results are encouraging even though highly preliminary due to the short nature of the program. Particulates were nearly completely removed and 99+% of the feed Na and K were removed.

Removal of chlorine fed as NaCl, was much less effective than alkali removal and it appeared as HCl in the product gas. This indicates that chemical trapping of Na by reaction with acidic ash components may play an important role in the alkali fume removal process.

H. Process Improvement Studies

Preliminary experiments were conducted to evaluate several potential process improvements as follows:

1. Use of the Chance reaction product as an H_2S acceptor in an entrained-type gas desulfurizer.

2. Use of limestone-based acceptors in the partially or fully calcined form in the gas desulfurizer.

3. Use of a regeneration cycle in which H_2S is reacted with $CaSO_4$ to produce a liquid Claus feed having a 2:1 $H_2S:SO_2$ ratio.

Experimental difficulties plagued the attempt to evaluate the first scheme. It therefore cannot be definitely ruled out of contention.

The second system appears to be of little interest due to chronic problems with acceptor agglomeration in the gas desulfurizer.

The third system was shown to be chemically feasible.

J. Environmental Evaluation

The process is very effective in removing sulfur, i.e., the sulfur dioxide produced by combustion of the cleaned producer gas amounts to only 20% of the 1.20 lb/MM Btu standard.

No data are available regarding the NH_3 content of the cleaned producer gas and the NO_x level in the flue gas after combustion.

Particulate removal effectiveness remains to be established in a pilot scale. The results given here support the conclusion that alkali fumes would be efficiently removed with the particulates.

The major waste solid product is the spent dolomite. The Chance reaction is shown to be effective for removal of potential H_2S pollution from the CaS contained in the spent solids.

One of the favorable characteristics of the process from the point of view of cooling water requirements and resource utilization is its high thermal efficiency.

II. CONCLUSIONS AND RECOMMENDATIONS

A. General Status of Development

The economic evaluation shows that the process is attractive with respect to alternative wet gas cleanup processes. The major elements of the process have been thoroughly proven out on a laboratory and continuous bench scale. It is, therefore, strongly recommended that pilot-scale development of the process be undertaken.

The major technical uncertainties that exist can only be resolved on a pilot plant scale. These are:

1. Equipment development required to remove residual particulate and alkali fumes (at 1600°F or higher) to a level compatible with subsequent use of the gas to power a gas turbine.
2. The level of NH_3 in the cleaned gas, and its impact on generation of NO_x on subsequent composition;
3. The effectiveness of operation on a large scale of the hardening system proposed for the pilot plant.

Continuing laboratory and bench-scale work is also recommended simultaneous with pilot scale development to effect optimization and process improvements and an improved understanding of the process fundamentals.

B. Continuous Cycling Studies with Dolomites

The main conclusion from these studies was that all features of the process have been confirmed.

Broad extension of the process, however, required development of a prehardening step such that naturally soft dolomites can be used. A hardening step was successfully developed which has no significant effect on the capital cost of the process. It was observed, however, that the prehardening step in some cases had a small deleterious effect on acceptor life. This necessitated an increase in make up requirements in the process economic study from the one percent previously employed to two percent.

The effect of desulfurizer temperature has been only partially studied in previous work and residence time was not studied at all. The improved acceptor life obtained in the batch cycling tests at shorter residence times provides a great incentive to confirm this beneficial effect in continuous bench-scale work.

All of the prior continuous work was also carried out at 1600°F and 1650°F. The modified process design presented here calls for an increase in desulfurizer temperature to 1675°F. Further studies in the continuous unit should therefore be conducted to tie down the effects of shorter residence times and higher temperatures in the gas desulfurizer.

C. Batch Kinetic and Cycling Studies

The outstanding result was that mentioned above, i.e., that reduced residence times in the desulfurizer improved acceptor life.

Another result on the negative side is the finding that reactivation of spent acceptors by high temperature regeneration is not a viable process. The "new" $CaCO_3$ thus formed is largely inactive in the regenerator.

Valuable data were obtained in the kinetic study, but they were insufficient in scope. It is recommended that this effort be continued with the aim of constructing a mathematical model of the process useful for design and scale-up purposes.

D. Chance Reaction Studies

Experimental work carried out on the disposal of spent acceptor via the Chance reaction confirmed the major features of the design assumptions used in the feasibility study. No further work is required short of pilot plant demonstration.

E. Liquid-Phase Claus

The major design features of this essential unit operation were confirmed by previous work given in the last annual report.(1) Further bench-scale work is desirable, though not essential, to provide additional kinetic data for mathematical modeling and scaleup.

F. Properties of Product Solids

Data were obtained which shed valuable light on the mechanism of acceptor deactivation. These data were obtained by a variety of physical and instrumental techniques.

These techniques should be further developed in conjunction with pilot plant development of the process.

G. Hot Removal of Particulates and Alkali

Encouraging results were obtained in preliminary work conducted on the above problem. Confirmation of the effectiveness of the process can only be obtained on a pilot plant scale.

Supporting laboratory and literature researches are, however, recommended to investigate the kinetics and thermodynamics of chemical trapping of alkali chloride vapors by reaction with acidic oxides present in coal ash.

H. Process Improvement Studies

Three systems were evaluated as set forth in the summary. The use of limestone in the process, even in the calcined form, appears to be of no interest.

The use of the Chance reaction product and production of a liquid-phase Claus feed by reaction of H_2S with $CaSO_4$ merit further laboratory investigation and such is recommended.

J. Environmental Evaluation

The process is highly effective for the original environmental purpose visualized, i.e., removal of sulfur at a high level of thermal efficiency.

No outstanding environmental disadvantages are apparent. An unresolved question, however, is the level of ammonia in the cleaned gas and its impact on ultimate NO_x emissions.

The above and other environmental questions with regard to particulate control and trace elements disposition can be answered only by pilot plant development.

III. ECONOMIC EVALUATION

A. Introduction

The purpose of the economic evaluation is to re-evaluate the cost of desulfurization via the proposed commercial gas desulfurization process. The desulfurization cost was evaluated in the initial feasibility study(2) wherein the process was fully described. The economic study as in the previous study(1) is restricted to the costs of desulfurizing the producer gas, including sorbent regeneration and sulfur recovery. The cost of gasification and the cost associated with generating electrical power from the desulfurized gas are not included in this economic review.

The most attractive end use of clean, pressurized, hot producer gas in the long term is in the integration with a combined cycle power station. However, since the scope of this evaluation was limited to the desulfurization step, the commercial evaluation is based on a more immediate practical objective: to supply a desulfurized fuel gas to a conventional, gas-burning power station with an approximate rating of 1400 MW. With respect to the total heat content of gas, this is the same plant size that was considered in the initial feasibility study.(2)

The economic re-evaluation is based on reflecting changes in the technical design basis since the first study was made as well as effect of escalation in costs due to inflation.

The design changes are the result of the experimental work conducted since the last study was made. The principal items are the following:

1. Acceptor makeup rate has been increased from 1% to 2% of the circulation rate.

2. A third stage collector has been added to remove residual alkali fumes and particulate matter prior to expansion of the gas.

3. The composition and temperature of the gas entering the gas desulfurizer has been changed to reflect new data on gasification kinetics.

B. Summary

The economics for the commercial design are based on an arbitrary start-up date of January, 1980, and are summarized in Table III-1.

The 1980 investment cost of the plant facilities to desulfurize producer gas under pressure by this process is approximately $58 per installed KW, and the operating costs correspond to about 2.9 mills/KWH of power generated.

A direct comparison with the economics previously presented in the December 1973 report(1) is also summarized in Table III-1. For consistency, the costs and capital charges of the previous design have been updated to reflect a July, 1975, base point with a January, 1980, start-up date. The purpose of this

TABLE III-1

Summarized Economic Evaluation
Regenerative Acceptor Desulfurization Process
70% Plant Operating Factor (6132 hours/year)

	Proposed Design	Adjusted(1) Economics of Previous Design
Coal Required:		
MM tons/year (6% Moisture)	3,414,000	3,428,000
Higher Heating Value, Btu/year	81.81×10^{12}	81.71×10^{12}
Producer Gas to Station (after expansion):		
Mols/hour	836,679	819,700
Temperature, °F	680	660
Pressure, psig	10	10
Higher Heating Value, Btu/year	63.76×10^{12}	65.19×10^{12}
HHV + Sensible Heat Content,(2) Btu/year	66.84×10^{12}	68.68×10^{12}
Desulfurization Plant Investment,(3) Total, MM	81.8	74.8
Desulfurization Plant Investment, $/KW	88.0	83.4
Desulfurization Cost:		
$/ton Feed Coal	7.40	6.61
¢/MM Btu HHV of Feed Coal	31.0	27.3
¢/MM Btu HHV of Product Gas	40.3	34.9
¢/MM Btu (HHV + Sens. Heat) Product Gas	38.0	32.6
Total Power Generated by Expander, megawatts(4)	340	317
Power Required for Compression of Process Air for Gasification Plant, megawatts(5)	170	157

(1) Previous design economics of "hot" cyclones only case, Reference 1 updated to reflect 1975 costs and projected escalation, interest rates and operating rates to 1980.
(2) Sensible heat content above an assumed air heater outlet temperature of 300°F.
(3) January, 1980 operation. Includes escalation and interest during construction. Does not include gasification plant or coal cost.
(4) Assuming 91% of the isentropic efficiency for the expander (see Reference 3).
(5) Assuming 89% of the polytropic efficiency for air compressors.

comparison is to illustrate that the higher incremental costs of the proposed design are mostly due to escalation and inflationary factors realized since the July, 1973, evaluation rather than to design changes. The design changes which have the most impact on the present economics are: 1) acceptor make-up requirements have been increased from 1% to 2% of the acceptor recirculation rate, and 2) a third stage particulate removal system has been added.

A sensitivity analysis on the economics reveals the desulfurization process is sensitive to total investment costs, utility rates, and sulfur credits while fairly insensitive to dolomite costs, escalation rates and interest rates within the realistic range of these variables.

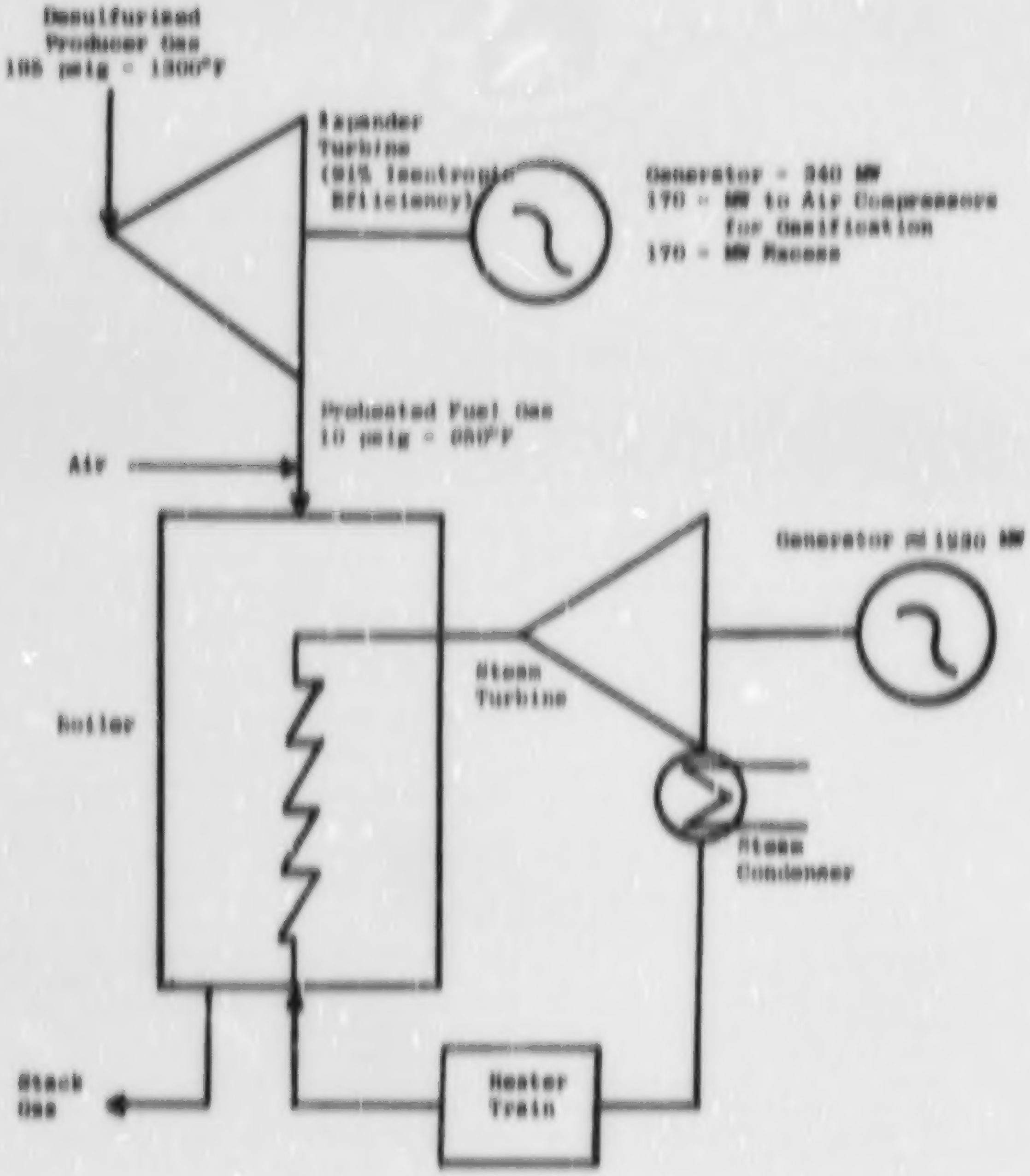
As indicated in Table III-1, the pressurized producer gas is expanded from system pressure (about 200 psig) to 10 psig through an expanding turbine to generate 340 megawatts of power. The power output from this unit exceeds the power requirement to compress the air for the coal gasification step. The excess power so recovered is included within the net 1400 MW capacity of the power station. This portion of the total station output would be produced at a higher efficiency than that produced via the conventional steam cycle. Consequently, the incremental reduction in the power station costs resulting from this higher efficiency could be a substantial credit to the desulfurization process. This credit has not been taken in this economic evaluation.

After expansion to 10 psig, the gas is delivered to the power station at a preheated temperature of 800°F. This sensible heat content serves to improve the efficiency (or the heat rate) of the station proper. In a conventional gas-burning station, the fuel gas is delivered at ambient temperature, and sensible heat from the products of combustion is recovered (via combustion air preheat) to an air heater exit temperature of about 300°F. Therefore, it seems reasonable to credit the process with the excess producer gas sensible heat above 300°F as an approximate means of measuring the improvement in the power station efficiency. As shown in Table III-1, the credit to the process for this excess sensible heat is about 2.3¢/MM Btu or about 6% of the system cost. It must be emphasized, however, that it is beyond the scope of this contract to define the actual dollar value of these power credits. (Refer to Figure III-1 for a schematic interpretation of the expander turbine plus conventional boiler and steam cycle.)

The economics presented in Table III-1 also apply for the case where a hard, active naturally occurring dolomite stone is not locally available and it is economically advantageous to artificially harden a local stone. It has been shown experimentally that soft stone can be hardened without losing activity. It is proposed that the hardening step could be accomplished in one gas desulfurizer by injecting the entire make-up dolomite stone into a draft tube with a stream of air. In the draft tube the stone is partially sulfided, oxidized to $CaSO_4$, and then reduced back to the sulfide form to complete the hardening process. As shown in Section II, since the process conditions and the total producer gas composition are essentially equivalent to the natural, hard stone case, the process economics are not significantly affected by the minor process design modification discussed above. It must be emphasized that all the experimental hardening studies were done in a two-stage process with the oxidation step being accomplished in a vessel external to the desulfurization process. Consequently, there is some technical uncertainty concerning the residence time involved with artificially hardening a dolomite stone in a draft tube of a desulfurizer.

FIGURE III-1

Simplified Schematic of Expander Turbine
plus Conventional Boiler and Steam Cycle.
Approximate Total Rating of Power Station = 1400 MW


Desulfurized
Producer Gas
185 psig - 1300°F
Expander
Turbine
(91% Isentropic
Efficiency)
Generator - 340 MW
170 - MW to Air Compressors
for Gasification
170 - MW Excess
Preheated Fuel Gas
10 psig - 880°F
Air
Generator ≈ 1230 MW
Steam
Turbine
Boiler
Steam
Condenser
Heater
Train
Stack
Gas

A few other areas of technical uncertainty still exist. It remains to be demonstrated that particulate matter and alkali content of the producer gas may be removable to acceptable levels by cyclonic devices alone. A "wet scrubbing" system at the sacrifices of higher desulfurization costs and reduced power recovery may be required to insure a "clean" feed gas to the turbo expander. Furthermore, without a "wet scrubbing" system the ammonia content of the gas is not reduced. Thus, the hot clean-up system will result in higher NO_x emissions from the power plant although the magnitude of the increase, due to failure to remove ammonia, cannot be readily estimated.

C. Process Description

Scope

The scope of work under this contract covers the experimental development and economic evaluation of a novel process for desulfurizing pressurized producer gas as a fuel to a power station. The simple block flow diagram in Figure III-2 defines the various steps in the overall process. Design and evaluation of coal preparation (crushing and sizing), and of coal gasification (Sections 100 and 200, respectively), are not covered in this study. Section 300, sulfur removal, and Section 400, sulfur recovery have been completely evaluated and form the substance of this report.

A relatively small quantity of make-up CO_2 is required in the process (Section 500). The CO_2 could be recovered either from a slip-stream of the desulfurized producer gas before power generation, or from a portion of the power station stack gas. Preliminary cost studies indicate approximately equal costs for the two alternative locations. For the purposes of this study, it is assumed that the make-up CO_2 is recovered from the pressurized producer gas before delivery to the power station. A standard hot potassium carbonate system is assumed to establish capital cost and utility requirements.

Sulfur Removal

A schematic flow diagram of the proposed commercial embodiment of this gas desulfurization process is shown in Figure III-3 (CCDC Drawing No. AF-3667).

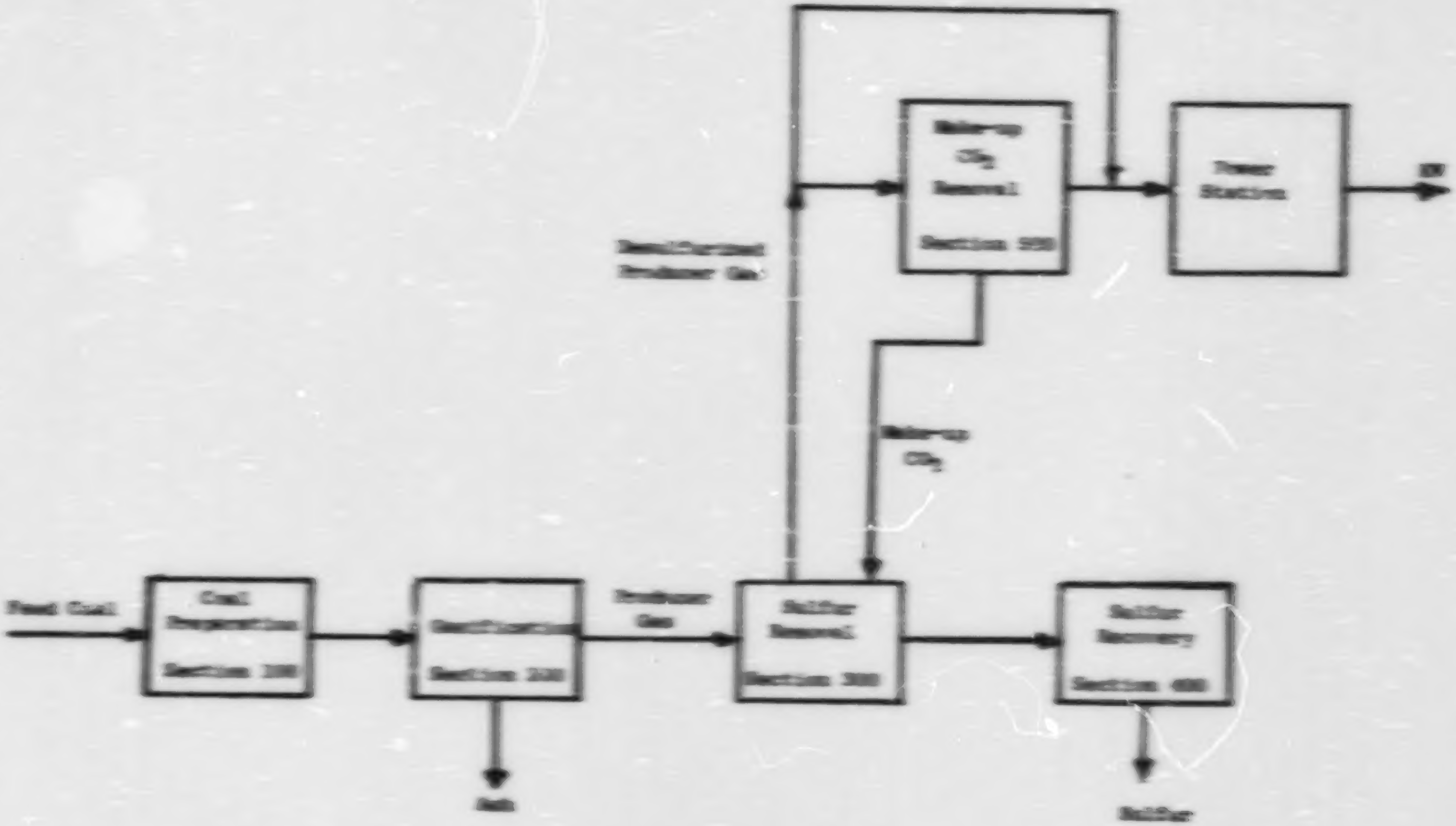
Gasifier product gas (Stream No. 4) flows to the bottom of a fluidized gas desulfurizer (D-301). The gas fluidizes a bed of sized dolomite at a temperature of 1670°F and at 15 atm. absolute pressure. Most (90%) of the H_2S in the gasifier gas reacts with the $CaCO_3$ component of the dolomite as follows:

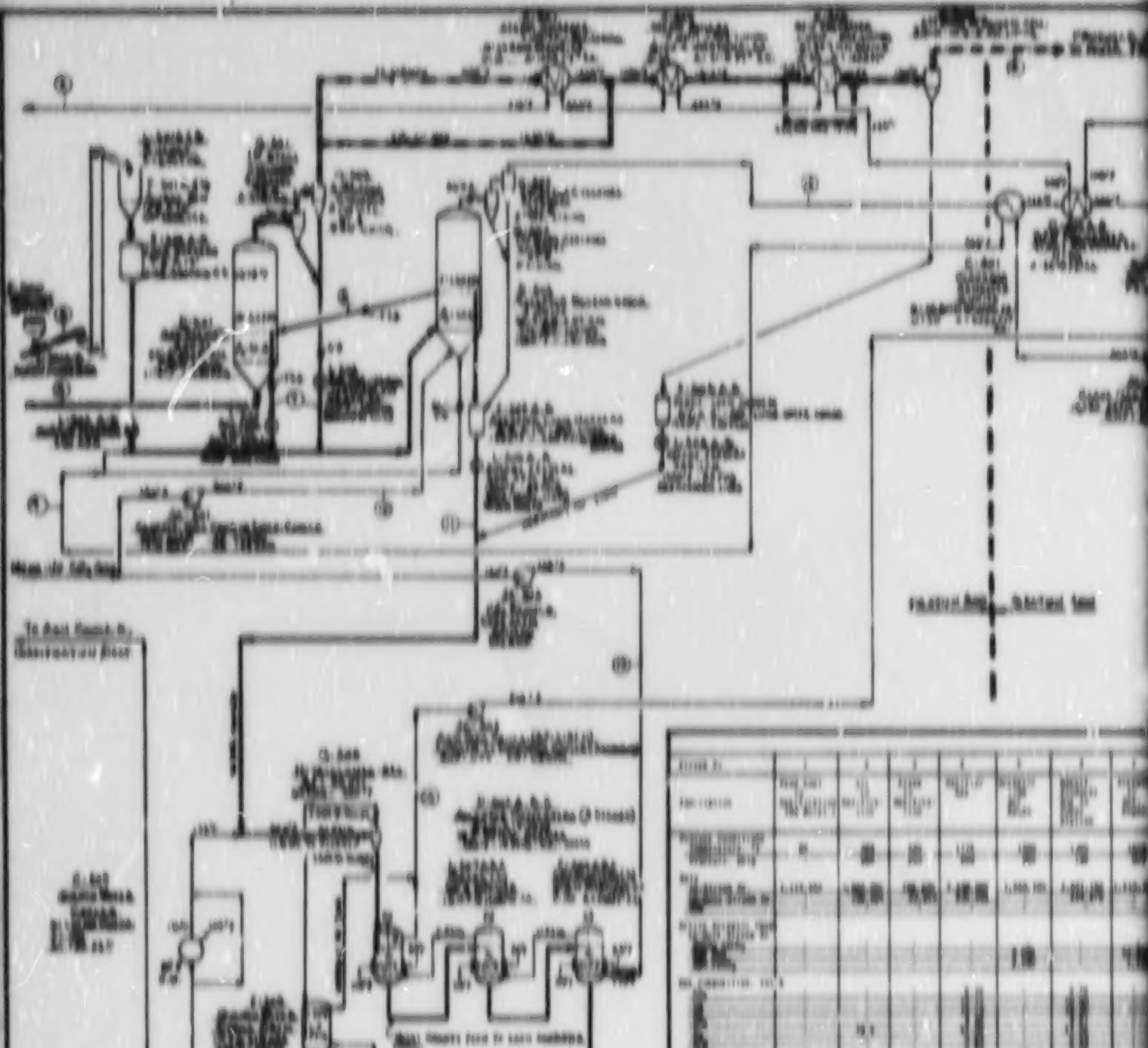
$$H_2S + MgO \cdot CaCO_3 = MgO \cdot CaS + CO_2 + H_2O.$$

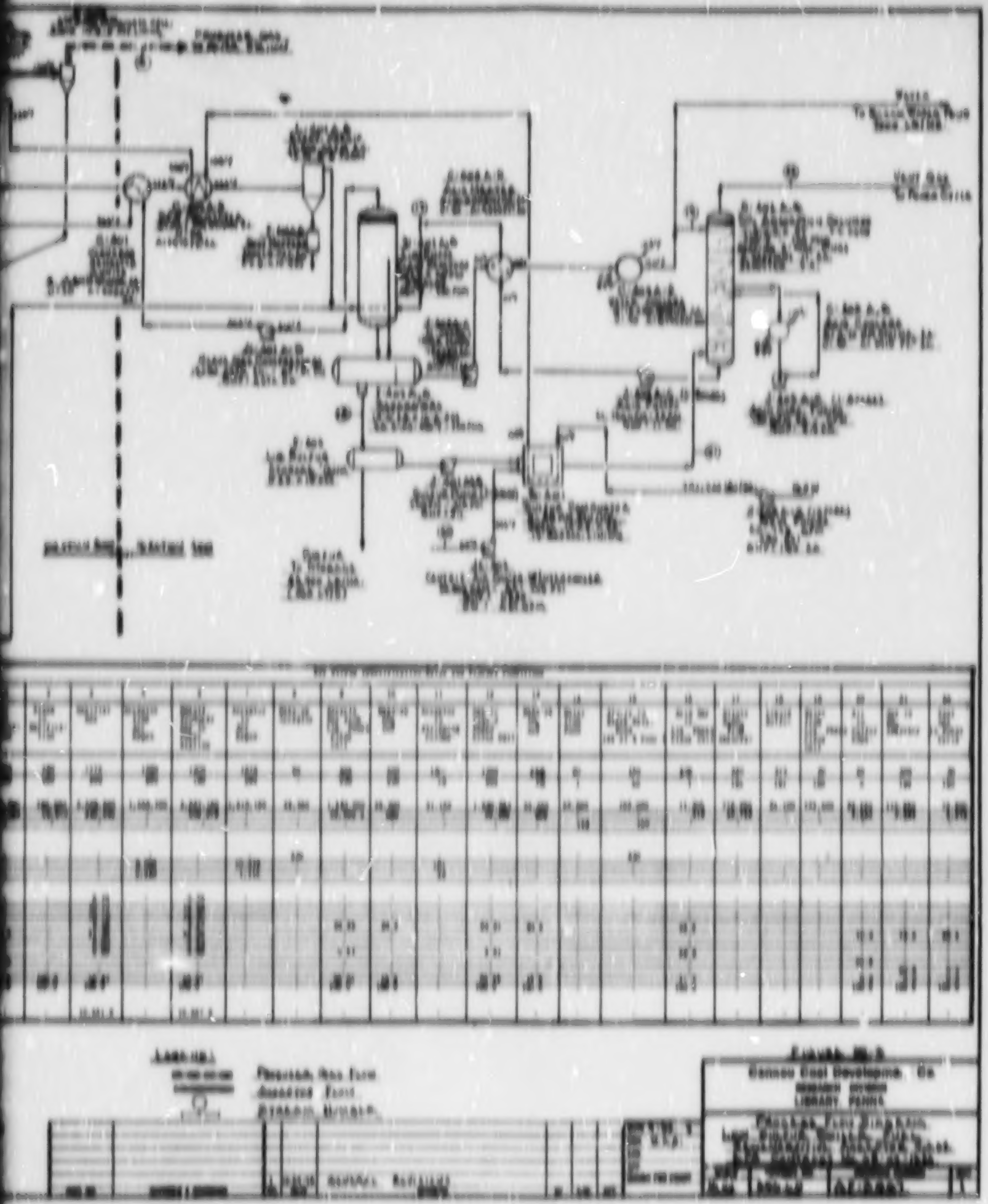
The desulfurized gasifier gas then passes through two stages of cyclones (C-301 and C-302, respectively) to remove substantially all of the fines including attrited acceptor and entrained ash. A portion of the sensible heat content of the desulfurized gas is used to preheat boiler feed water and to generate and superheat the steam required for gasification of the feed coal in heat exchangers E-303, E-302, and E-301, respectively. Any potential alkali compounds formed at the lower gas temperatures are removed via a third stage particulate collector, which also serves as a final process clean-up step. The desulfurized producer gas at 1300°F and 210 psia (Stream No. 6) is then delivered to the power station. Subsequent use of this gas is dependent on the design of the power station, and is discussed in other sections of this report.

FIGURE III-1

Block Flow Diagram - Overall System


Feed Coal
Coal Preparation
Section 100
Gasification
Section 200
Ash
Producer Gas
Sulfur Removal
Section 300
Sulfur Recovery
Section 400
Sulfur
Desulfurized Producer Gas
Make-up CO_2
Make-up CO_2 Removal
Section 500
Power Station
KW





Regenerated acceptor (Stream No. 5) at 1300°F is continuously charged to the gas desulfurizers by gravity feed. The sulfided acceptor is pneumatically conveyed by a portion of the required recycle gas (Stream No. 9) to fluidized acceptor regenerators (D-302). Make-up acceptor (Stream No. 8) is introduced into the system by a lockhopper system comprised of L-301, F-301, F-302, and L-302. This small stream is also pneumatically conveyed to D-302 by means of recycle gas. Make-up CO_2 required in D-302 (Stream No. 10) is pressurized by JC-301 and charged to D-302.

The fluidized acceptor regenerators (D-302) are maintained at 1300°F and 15 atm. absolute pressure. The sulfided acceptor is recarbonated at these conditions by the reverse reaction,

$$MgO \cdot CaS + CO_2 + H_2O = MgO \cdot CaCO_3 + H_2S.$$

The carbonated magnesium component of the make-up acceptor is also calcined at these conditions,

$$MgCO_3 \cdot CaCO_3 = MgO \cdot CaCO_3 + CO_2.$$

Spent acceptor (2% of the circulating flow) is withdrawn from the regenerators via a lockhopper, F-304, and a rotary feeder, L-306 (Stream No. 11). This spent acceptor must be treated before disposal. Over 75% of the calcium component of this stream is in the form of CaS. If this were disposed of directly to the station ash pit, H_2S gas would slowly evolve as the CaS was hydrolyzed. To avoid this condition, the spent acceptor is directly contacted with CO_2 and water in three stages of stirred reactors, D-303, to convert the CaS to $CaCO_3$. At these conditions, the MgO component of the dolomite would also recarbonate. The overall reaction is,

$$MgO \cdot CaS + 2\ CO_2 + H_2O = MgCO_3 \cdot CaCO_3 + H_2S.$$

The spent acceptor is conveyed hydraulically by a dilute recirculating slurry stream to hydroclones, G-306. The underflow slurry (controlled at 35 wt. % solids) flows to the three series converters or Chance reactors, D-303A, B and C, respectively. Each converter is agitated by a turbine-type mixer, L-307, and some reaction heat is removed in each stage by coolers, C-304. The spent acceptor, stripped of sulfur and fully carbonated, is pumped, J-301, to the station ash pit. The overflow slurry from hydroclone, G-306, is continuously recirculated via surge drum, F-305, and circulating pump, J-303. The sensible heat content from the spent acceptor is removed by mixing with 90°F make-up black water and by cooling in C-305. The make-up water is pumped from the station pond overflow via J-302 (which also supplies water to cool the gasifier ash and convey it to the station ash pond).

Acid gas resulting from the acceptor stripping operation (Stream No. 16) is compressed, JC-302, to the liquid-phase Claus reactor pressure.

Sulfur Recovery

The process gas exiting the regenerators (Stream No. 12) is passed through two stages of cyclones, G-304 and G-305, to remove entrained acceptor. The sensible heat content of this stream is then exchanged with recycle gas in

C-401, and with boiler feed water (required for gasification steam) in C-402. Electrostatic precipitators, L-401, are provided to remove all entrained dust. The gas then flows to the bottom of the liquid-phase Claus reactor, D-401.

The concentration of H_2S in the gas from the acceptor regenerators is 88% of the equilibrium restriction at 1300°F and amounts to only about 3.6 volume percent. The liquid-phase Claus reaction developed in this work is uniquely suited to processing this gas. The liquid-phase Claus reactors, D-401, operate at 310°F and about 210 psia. Product gas from the acceptor regenerators (Stream No. 12), gas from the reject acceptor stripping section (Stream No. 16), and dilute aqueous H_2SO_3 (Stream No. 17) are charged to the bottom of the liquid-phase Claus reactors. Flow is upward through a sparged reactor containing only aqueous sulfurous acid as was demonstrated during the experimental work described in the previous report.(1) Liquid sulfur is produced by the reaction,

$$2\ H_2S + H_2SO_3 = 3\ S + 3\ H_2O.$$

Liquid sulfur and liquid water flow from the reactor to decanter-type separators, F-402. Unreacted gas (Stream No. 9), saturated with water vapor at 310°F, is compressed by JC-401, reheated in exchanger, C-401, to 935°F and returned to the acceptor regenerator reactors. The sensible heat content of the liquid water from F-402 (Stream No. 19), is exchanged with the feed acid (Stream No. 17) in C-403, further cooled to 90°F in C-404, and charged to the SO_2 absorption towers, D-402. A slip stream of water is rejected to the black water pond to maintain water balance.

Approximately one-third of the sulfur from F-402 is burned with stoichiometric air (Stream No. 20) to produce SO_2 in the pressurized combustor, B-401. Excess heat is removed to boiler feed water via cooling tubes in the walls. The exit gas from the sulfur combustor (Stream No. 21) flows to the base of the SO_2 absorption towers, D-402. Water (Stream No. 19) flowing down through the packed towers absorbs the SO_2 in the gas by,

$$SO_2 + H_2O = H_2SO_3 \text{ aqueous.}$$

Most of the exothermic heat of reaction is removed by side stream coolers, C-405. The vent gas from the absorption towers (Stream No. 22) is at 90°F and 205 psia. It probably would contain some residual SO_2 (assumed in this case as 0.3 volume percent). The most practical means of disposing of this gas is to bleed it to an intermediate stage of the expansion turbine required for the desulfurized producer gas in the power station. This would decrease the net sulfur removal efficiency of this process from 95.9% to 95.3%, but would increase the power output of the station slightly and would eliminate an entire stack gas scrubbing installation following the SO_2 absorption step.

D. Design Basis

Gasification

Although the detailed design and evaluation of the gasification system is not covered in this study, it is of interest to at least relate the composition of the raw gasifier gas to the input feed streams of the gasification section.

1. Feed Coal

This study is based on the use of a high-sulfur content, highly caking Pittsburgh Seam coal. The analyses of a typical coal (Ireland Mine) of this seam is shown below:

Feed Coal Analysis

Moisture, as received, Wt. %	6.0
Ultimate Analysis, MF basis, Wt. %	
Hydrogen	4.8
Carbon	69.8
Nitrogen	1.2
Oxygen	7.6
Sulfur	4.3
Ash	12.3
Higher Heating Value, MF basis	12,700 Btu/lb

2. Other Design Constraints

The total sensible heat content of the gasifier steam is supplied by heat exchange within the sulfur removal and sulfur recovery sections. Additional design constraints for the fluidized bed gasifier and carbon burn-up cell are:

System Pressure	15 atm
Gasifier Temperature	1775°F
Fixed Carbon Gasification Rate	0.0037 lb C/min-lb C in bed
Steam Conversion in Gasifier	44.2%
Burn-up Cell Temperature	1800°F
Percent Total Carbon to Burn-up Cell	16.4%

Gas Desulfurizer

The sulfur in the producer gas (as H_2S) is removed in the gas desulfurizer by reaction with $CaCO_3$ as follows:

$$MgO \cdot CaCO_3 + H_2S = MgO \cdot CaS + CO_2 + H_2O.$$

The commercial design basis for this study is adopted from the actual experimental data which are reviewed in a later section of this report. Pertinent design values are:

Desulfurizer Temperature	1870°F
Desulfurizer Pressure	15 atm
Avg. Acceptor Size, Dp arithmetic mean	0.065 inch
Acceptor Density, ρ_s	130 lb/CF
Mol % Ca as CaS - Inlet Acceptor	78.6%
Mol % Ca as CaS - Outlet Acceptor	90.3%
$\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ Out - $\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ In	0.117
Avg. Acceptor Residence Time	20 min.
Outlet Fluidizing Velocity	3.4 ft/sec
Approach to Equilibrium $(H_2O)(CO_2)/H_2S$	100%
Removal of H_2S from Producer Gas	95.8%
CO_2 Driving Force	0.147 atm(a)

(a) p_{CO_2} - equilibrium p_{CO_2} for the reaction, $CaCO_3 = CaO + CO_2$.

Acceptor-Regenerator

The highly-sulfided acceptor from the gas desulfurizer is regenerated (converted to $CaCO_3$) at a lower temperature by the reverse reaction,

$$MgO \cdot CaS + CO_2 + H_2O = MgO \cdot CaCO_3 + H_2S.$$

Note that small yields of CO and COS were actually detected in the experimental program, and S_2 was found in the exit gas piping when the gas was deficient in hydrogen. These trace constituents have been ignored in the economic evaluation.

The acceptor make-up requirement was arrived at by extrapolation of data from the continuous unit. It was found experimentally that the acceptor activity declined exponentially with number of cycles. The sulfur absorption was assumed to involve 11.7% of the total calcium. The rate of decline was sufficiently small to select 2% make-up rate.

The required make-up acceptor (as $MgCO_3 \cdot CaCO_3$) is charged to the acceptor-regenerator. The $MgCO_3$ component of the dolomite is completely calcined at these conditions as follows:

$$MgCO_3 \cdot CaCO_3 = MgO \cdot CaCO_3 + CO_2.$$

Other pertinent design values for the commercial acceptor-regenerator are:

Regenerator Temperature	1300°F
Regenerator Pressure	15 atm
Avg. Acceptor Size, Dp arithmetic mean	0.065 inch
Acceptor Density, ρ_s	132 lb/CF
Mol % Ca as CaS - Inlet Acceptor	90.3%
Mol % Ca as CaS - Outlet Acceptor	78.6%
$\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ In - $\left(\frac{\text{Mols CaS}}{\text{Mols Ca}}\right)$ Out	.117(a)
Avg. Acceptor Residence Time	60 min.
Outlet Fluidizing Velocity	1.50 ft/sec
Approach to Equilibrium, $(H_2O)(CO_2)/H_2S$	88%

(a) Excluding make-up acceptor.

Acceptor Converters (Chance Reactors)

In this process the spent acceptor to be rejected from the system must be converted from MgO·CaS to $MgCO_3 \cdot CaCO_3$ before disposal. In the unconverted state, the acceptor would slowly release H_2S to the atmosphere.

The conversion is by the chemical reaction,

$$MgO \cdot CaS + 2\ CO_2 + H_2O = MgCO_3 \cdot CaCO_3 + H_2S.$$

The design of the acceptor converters was based on actual experimental data described in Section XII, plus on work done by the Bureau of Mines staff at Salt Lake City.

Pertinent design values are:

Conversion Temperature	200°F
Conversion Pressure	Atmospheric
Wt. % Acceptor in Slurry	45
Total Residence Time	60 min.
No. Stages Required	3
Utilization of CO_2	80%
Conversion of CaS to $CaCO_3$	Approaching 100%

Liquid-Phase Claus

The offgases from the acceptor regenerators and the acceptor converters are passed cocurrently through a reactor with a stream of aqueous H_2SO_3 where the following reaction occurs,

$$2\ H_2S + H_2SO_3 = 3\ S + 3\ H_2O.$$

The design basis is taken directly from the experimental results with approximately 20% excess volumetric space rate to insure a 90% conversion of H_2S to sulfur. Design values follow:

Reactor Temperature	310°F
Reactor Pressure	14 atm.
Volumetric Space Rate	1110 hr^{-1}
Avg. Vapor Residence Time	31 sec.

SO_2 Absorption

The dilute H_2SO_3 required in the liquid-phase Claus reactors is produced by absorption of SO_2 in water in standard countercurrent flow packed towers. The design is based on published data for the system.(4,5) Key design parameters are:

Absorber Temperature	80-110°F
Absorber Pressure	14 atm.
Liquid Rate	10,000 lb/hr-ft^2
Packing	3" porcelain rings
No. Stages	4
Outlet Vapor Velocity	0.20 ft/sec
Percent Flooding Velocity	50%

E. Material and Heat Balances

Basic to the process design and economic evaluation of this process on a commercial scale was the completion of mass and heat balances for each important processing step. The capacity of the plant in this study (with respect to the total heating value of the desulfurized producer gas above 60°F), is the same as in the initial feasibility study.(2) This plant would supply a modern conventional gas-fired power station of approximately 1400 MW rating.

The computer program developed by CCDC for the integrated system of coal preoxidation, gasification, carbon-burn-up cell and producer gas desulfurization was described in the last report.(1)

With these calculations as a starting point, the following mass and heat balances were evolved for the commercial process design:

Table III-2 - Gas Desulfurizer
Table III-3 - Acceptor Regenerator
Table III-4 - Acceptor Stripping Column
Table III-5 - Liquid-Phase Claus Reactor
Table III-6 - Sulfur Combustor
Table III-7 - SO_2 Absorption Column
Table III-8 - Overall Mass and Heat Balance

F. Plant Investment and Operating Cost Estimates

From the heat and material balances, a process flow sheet was developed as shown in Figure III-9 (CCDC Dwg. No. AF-3687). A preliminary capital cost estimate was developed by the CCDC Engineering Department for Sections 300 and 400, and is summarized in tabular form in Appendix A as Tables A-1 and A-2. Note that Section 500, the make-up CO_2 system was assumed to be a conventional "hot pot" system. A detailed estimate was not required since the costs and utility requirements are adequately defined in the literature.(8) Furthermore, costs that are not directly associated with desulfurization, i.e., air compressors for the gasifiers and the expander turbine, are not included in this desulfurization investment.

The capital cost estimates developed in Appendix A are defined as inside battery limits (ISBL). To these costs must be added off-site facilities (OSBL) which include utility costs, electric substations, cooling water towers, distribution piping and boiler feed water treating. The accuracy of the capital cost estimates in this study is estimated as ± 25%.

It was necessary in this study to project escalation in the plant investment and operating costs to reflect a presumed start-up date of January, 1980. This work was based upon the following assumptions:

1. July, 1975 costs as a base point.
2. Begin design and construction, January, 1976.
3. Begin operations, January, 1980.
4. Escalation at 9-1/2% per year average of construction labor and material.
5. Interest during construction at 8-1/2% simple interest on cash flow.
6. Escalation of direct operating labor at 7% per year.
7. Interest on working capital at 8-1/2% per year.

[illegible]

[illegible]
[illegible]

[illegible] [illegible] [illegible] [illegible]

[illegible]	[illegible]	[illegible]	[illegible]	Temp. [illegible]	[illegible]	[illegible]
[illegible] [illegible]						
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]
Sub-Total	[illegible]	[illegible]	[illegible]			[illegible]
[illegible] [illegible]						
[illegible]	[illegible]	[illegible]	—	[illegible]	—	[illegible]
[illegible]	[illegible]	—	—	[illegible]	—	[illegible]
Sub-Total	[illegible]	[illegible]	—			[illegible]
[illegible] [illegible]						
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Sub-Total	[illegible]	[illegible]	[illegible]			[illegible]
[illegible] [illegible]						
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Sub-Total	[illegible]	[illegible]	[illegible]			[illegible]
[illegible]						
[illegible]						[illegible]
Totals	[illegible]	—				[illegible]
[illegible]						
[illegible] [illegible]						
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]
Sub-Total	[illegible]	[illegible]	[illegible]			[illegible]
[illegible] [illegible]						
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]			[illegible]
[illegible] [illegible]						
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Sub-Total	[illegible]	[illegible]	[illegible]			[illegible]
[illegible]						
[illegible]						[illegible]
[illegible]						[illegible]
Totals	[illegible]	—				[illegible]

Note: [illegible]
[illegible]

Table III-4

Mass and Heat Balance
Acceptor Stripping Column

Basis: 1 Hour Datum: 60°F, H_2O (ℓ)

	Lb.	Mols	Temp. °F	ΔH or Cp	ΔH MM Btu
Input					
⑪ Acceptor from Acc. Regen.					
MgO CaS	20,300	181	1300	17,500 Btu/mol	3.17
MgO $CaCO_3$	6,900	49	1300	45,710 Btu/mol	2.24
Inerts	3,950	-	1300	300.65 Btu/lb	1.19
Sub-Total	31,150	230			6.60
⑬ CO_2 from External Source					
CO_2	22,650	514	238	1654 Btu/mol	.85
H_2O (v)	1,700	94	238	20,440 Btu/mol	1.92
Sub-Total	24,350	608			2.77
⑭ Water (ℓ)	58,800	-	90	30.03 Btu/lb	1.76
Heat of Reaction					
MgO CaS + CO_2 + H_2O = MgO $CaCO_3$ + H_2S (181 mols x 30,630 Btu/mol)					5.58
MgO $CaCO_3$ + CO_2 = $MgCO_3$ $CaCO_3$ (230 mols x 42,950 Btu/mol)					9.88
Totals	114,300	-			26.57
Output					
⑮ Reject Acceptor to Pond					
$MgCO_3$ $CaCO_3$	42,400	230	190	40.3 Btu/mol °F	.58
Inerts	3,950	-	190	0.21 Btu/lb °F	0.10
Water (ℓ)	56,650	-	190	[illegible] Btu/lb	[illegible]
Sub-Total	103,000	-			[illegible]
⑯ Acid Gas to Liquid Phase Claus					
CO_2	4,550	103	200	1287 Btu/mol	0.13
H_2S	6,150	181	200	1186 Btu/mol	0.21
H_2O (v)	600	34	200	1117 Btu/lb	0.67
Sub-Total	11,300	318			1.01
Heat Rejected to Cooling Water	------				22.86
Totals	114,300	-			26.57

Note: Circled numbers refer to Stream Number on [illegible] Dwg. AF-3667.
Temperature/Pressure may differ depending on location of
identifying flag.

Table III-[illegible]

Mass and Heat Balance
Liquid-Phase Claus Reactor

Basis: 1 Hour   Datum: 60°F, H_2O (l)

Inlet	Lb	Mols	Mol %	Temp. °F	ΔH or Cp	ΔH MM Btu
(15) Gas from Ammonia Regenerator						
CO_2	1,0[illegible]	[illegible].1	[illegible]	[illegible]	2,[illegible] Btu/Mol	[illegible]
H_2S	4[illegible],730	1,3[illegible].4	3.61	[illegible]	2,[illegible] Btu/Mol	3.0
H_2O (v)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] Btu/Mol	[illegible]
Sub-Total	1,[illegible],750	[illegible].3	100.00			[illegible]
(16) Gas from Ammonia-Stripping Column						
CO_2	4,[illegible]	[illegible]	[illegible]	[illegible]	2,[illegible] Btu/Mol	0.2
H_2S	[illegible]	[illegible]	[illegible]	[illegible]	2,[illegible] Btu/Mol	0.4
H_2O (v)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible],720 Btu/Mol	[illegible]
Sub-Total	11,[illegible]	[illegible]	100.00			1.3
(17) Liquid from SO_2 Absorber						
H_2SO_3	[illegible]	672.5	1.65	[illegible]	1.0 Btu/lb-°F	129.7
H_2O (l)	[illegible]	[illegible]	[illegible]	[illegible]		
Sub-Total	7[illegible]	[illegible],747.5	100.00			
Heat of Reaction						
$2\,H_2S + H_2SO_3 = 3\,S + 3H_2O$	(1365 mols H_2S x 42,[illegible] Btu/mol)					57.8
Totals	2,[illegible]	—				523.9
Outlet						
(9) Gas to Ammonia Regenerator						
CO_2	1,0[illegible]	[illegible].1	6[illegible]	[illegible]	2,[illegible] Btu/Mol	[illegible]
H_2S	[illegible]	[illegible].4	.41	[illegible]	2,[illegible] Btu/Mol	0.3
H_2O (v)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] Btu/Mol	[illegible]
Sub-Total	1,[illegible]	[illegible]	100.00			522.9
(18) Sulfur (l)	[illegible]	2,0[illegible]	—	[illegible]	0.2 Btu/lb-°F	[illegible]
Water (l)	[illegible]	[illegible]	—	[illegible]	251.88 Btu/lb	[illegible]
Heat Loss						1.3
Totals	2,[illegible]	—				523.9

Note: Circled numbers refer to Stream Number on [illegible] Dwg. [illegible].
Temperature/Pressure may differ depending on location of identifying Tag.

Table III-6

Mass and Heat Balance
Sulfur Combustor

Basis: 1 Hour   Datum: 60°F, H_2O (l)

	lb	Mols	Temp. °F	ΔH	ΔH MM Btu
Input					
Sulfur(s)	21,800	679.5	60	~	0
[illegible] **Air**					
O_2	21,750	679.5	485	3,044 Btu/Mol	9.85
N_2	71,600	2,556.2	485		
H_2O (v)	500	28.4	485	22,207 Btu/Mol	0.63
Sub-Total	93,850	3,264.1			10.48
Heat Required to Melt Sulfur and Preheat to 280°F					1.37
Heat of Reaction					
$S + O_2 = SO_2$ (679.5 mols x 127,690 Btu/Mol)					86.77
Totals	115,650				98.62
Output					
㉛ **Gas to Absorption Tower**					
SO_2	43,550	679.5	400	3,487 Btu/Mol	2.37
N_2	71,600	2,556.2	400	2,258 Btu/Mol	5.77
H_2O (v)	500	28.4	400	21,261 Btu/Mol	0.60
Sub-Total	115,650	3,264.1			8.74
Heat Transfer to B.F.W. Preheater					78.80
Heat Loss					11.08
Totals	115,650				98.62

Note: Circled numbers refer to Stream Number on CCIW Dwg. AF-3007. Temperature/Pressure may differ depending on location of identifying flag.

Table III-7

Mass and Heat Balance
SO_2 Absorption Tower

Basis: 1 Hour   Datum: 60°F, H_2O (l)

	lb	Mols	Temp. °F	ΔH or Cp	ΔH MM Btu
Input					
㉑ **Gas from Sulfur Combustor**					
SO_2	43,550	679.5	400	3,487 Btu/Mol	2.37
N_2	71,600	2,556.2	400	2,258 Btu/Mol	5.77
H_2O (v)	500	28.4	400	21,261 Btu/Mol	0.60
Sub-Total	115,650	3,264.1			8.74
⑱ **Water** (l)	733,500		90	29.96 Btu/lb	21.98
Heat of Reaction					
$SO_2 + H_2O = H_2SO_3$ (aq.) (672.5 mols x 13,720 Btu/Mol)					9.23
Totals	849,150	--			39.95
Output					
㉒ **Vent Gas**					
SO_2	450	7.0	90	285 Btu/Mol	*
N_2	71,600	2,556.2	90	195 Btu/Mol	0.50
H_2O (v)	150	8.8	90	19,328 Btu/Mol	0.17
Sub-Total	72,200	2,572.0			0.67
⑰ **Dilute H_2SO_3 to Claus Unit**					
H_2SO_3	55,200	672.5	101	1.0 Btu/lb - °F	31.85
H_2O (l)	721,750	40,075.0	101		
Sub-Total	776,950	40,747.5			
Heat Rejected to Cooling **Water**					7.43
Totals	849,150	--			39.95

Note: Circled numbers refer to Stream Number on CUDC Dwg. AF-3667.
Temperature/Pressure may differ depending on location of identifying flag.

[illegible] (continued)

[illegible]

Note: [illegible]

* [illegible]

The total investment summary for the proposed design is shown in Table III-9. The installed cost in July, 1976, dollars is $54,100,000. Escalation of these costs to January, 1980 (as defined above), increases the total investment to $61,200,000.

Direct operating costs are shown in Table III-10. Note, that an average plant operating factor of 70% or 6132 hours per year was assumed reflecting power station practice. The unit values used to develop operating costs are shown directly in Table III-10.

G. Evaluation of System Economics

Base Case

The first report on this project(8) clearly showed that the most economic application of this process is in combination with a combined cycle power station. This current work is more restricted in scope and is limited to a simple exposition of the costs of desulfurizing the pressurized producer gas.

Based on the cost estimates presented in the previous section, the process economics are estimated as shown in the first column of Table III-11. The net annual operating costs are $25.357 MM/year. Since 50% of this is represented by capital charges, the economics are very sensitive to the investment costs. Furthermore, at a value of $55.00/metric ton the sulfur credit is equivalent to about 11% of the annual operating costs.

Based on a dolomite make-up rate of 2% of the circulation rate and on a dolomite cost of $16/ton, the annual acceptor cost is about 9% of the net operating cost. The 1980 acceptor cost was derived by escalating a 1976 quoted price of a 4 x 16 mesh dolomite stone delivered by rail from Thornton, Illinois to Hillsboro, Illinois. The 1980 based dolomite cost includes the investment charge (at 15%/yr) of installing a rail spur and unloading facilities at the Hillsboro location. Per recommendation of the dolomite supplier, the cost of raw stone was escalated at 8%/yr. Transportation cost was escalated at 9-1/2%/yr. In the event that a hard, active naturally occurring dolomite is not locally available, it may be preferable to artificially harden a local stone to minimize the make-up acceptor costs (refer to Hardening discussion in Section H).

The system costs presented in Table III-11 are more meaningful if related to the coal required for the total system, or to the heating value of the gas delivered to the power station. The net annual operating costs are equivalent to $7.40/ton of feed coal and 31.0¢/MM Btu HHV of the coal.

Considering only the higher heating value of the product gas to the power station, the corresponding cost of desulfurization is 40.3¢/MM Btu. Allowing for the sensible heat credit above 300°F as discussed earlier, the desulfurization cost is reduced to 38.0¢/MM Btu, or a reduction of about 6%.

Another credit to the process is the power generated by the expanding turbine-generator set that is in excess of that required by the gasification air compressors. As noted previously, it is beyond the scope of this contract to determine the actual dollar credit associated with this higher efficiency generated power. However, to at least qualitatively show the potential impact

Table III-9

Investment Summary

Plant Section	300 Sulfur Removal	400 Sulfur Recovery	500 Make-up CO_2 System	Total
Utilities Required				
Electricity, kW	2,470	10,285	340	13,100
Cooling Water, gpm	2,975	7,746	16,000	26,719
Low-Pressure Steam, lb/hr	x	x	79,300	79,300
Boiler Feed Water, gpm	x	1,584	x	1,584
Operating Labor Required				
Men/Shift	4	3	1	8
Investment	(in $1000)			
Erected Cost (ISBL)	24,020	16,700	5,000	45,700
Off-sites & Utilities (OSBL)				
Off-sites	1,666	1,100	300	3,000
Electrical	310	2,200	-	2,500
Cooling Water	200	500	1,000	1,700
Boiler Feed Water	x	1,300	x	1,300
Misc. Utilities	300	300	100	900
Total OSBL	2,400	4,400	1,400	8,402
Installed Plant Cost (July, 1975)	26,600	21,100	6,400	54,100
Escalation to Jan. 1980				14,100
Sub-Total				68,200
Interest during Construction				13,000
Total Investment (Jan., 1980)				81,200

Table III-10

Direct Operating Cost Summary Excluding Acceptor Cost

Basis: 70% Plant Operating Factor

Plant Section	300 Sulfur Removal	400 Sulfur Recovery	500 Make-up CO_2 System	Total
Direct Operating Labor Man/Shift	4	3	1	8
Direct Operating Cost		(in $1000/yr)		
1. Operating Labor at $81,400/man/shift/yr	326	244	81	651
2. Maintenance Labor at 1.6% Installed Plant Cost	536	426	130	1,092
3. Direct Supervision 15% of 1 + 2	129	101	32	262
4. Indirect Overhead 50% of 1 + 2 + 3	495	386	122	1,003
5. Payroll Overhead 15% of 1 + 2 + 3 + 4	223	174	55	452
6. Maintenance Material 2.4% Installed Plant Cost	804	639	195	1,638
7. Miscellaneous Supplies 15% Maint. Material	121	96	29	246
8. Insurance & Taxes 2% Installed Plant Costs	670	532	162	1,364
9. Utilities				
Electricity at 55 mills/KWH	380	1,586	55	2,021
Cooling Water at 9¢/M Gal.	99	258	630	987
BFW at 85¢/M Gal.	0	496	0	496
Low-Pressure Steam $2.10/M lb	0	0	893	893
Chemicals & Catalysts (ex Acceptor)	0	0	27	27
Sub-Total Utilities	479	2,340	1,605	4,421
Total Direct Operating Cost (Jan. 1980)	3,783	4,937	2,407	11,127

Table III-11

Economic Evaluation
Regenerative Acceptor Desulfurization Process

Basis: 70% Plant Operating Factor (6132 hr/yr)

Case	Present Proposal	Previous Design "Hot" Cyclones Only
Coal Required		
Ton/yr (0% Moisture)	3,414,000	3,409,000
Higher Heating Value, Btu/yr	81.81×10^{12}	81.71×10^{12}
Desulfurized Producer Gas To Station		
Mols/Hr	836,078	813,701
Temperature	850°F	880°F
Pressure	10 psig	10 psig
Higher Heating Value, Btu/yr	65.78×10^{12}	65.19×10^{12}
HHV + Sensible Heat Content, Btu/yr(1)	88.54×10^{12}	88.60×10^{12}
Cost Analysis		
Installed Plant Cost (1978)	54.1 MM	49.8 MM
Escalation to 1980	14.1 MM	13.0 MM
Interest during Construction at 8% per year	13.0 MM	12.0 MM
Total Investment	81.2 MM	74.8 MM
Investment per Installed KW	$88.0	$83.4
Working Capital	2.75 MM	2.48 MM
Annual Operating Costs		
Direct Operating Cost (1980)	$11.137 MM/Year	$10.537 MM/Year
Acceptor at $10/ton	2.074 MM/Year	1.028 MM/Year
Interest on Working Capital at 8.5%	0.234 MM/Year	0.210 MM/Year
Capital Charges at 18% Investment	14.616 MM/Year	13.464 MM/Year
Sulfur Credit at $55/metric ton	($ 2.683 MM/Year)	($ 2.624 MM/Year)
Net Annual Cost	$25.378 MM/Year	$22.615 MM/Year
Desulfurization Cost Expressed:		
In terms of feed coal		
$/ton coal	7.43	6.65
¢/MM Btu HHV	31.0	27.7
In terms of product gas to station:		
¢/MM Btu HHV	38.6	34.8
¢/MM Btu (HHV + Sens. Ht.)(1)	28.6	25.5
Power Generated by Expander in Excess of Air Compressor Req'ts(2)	170 MW	160 MW

(1) Sensible heat content above an assumed air heater outlet temp. of 300°F.
(2) Assuming 91% of the isentropic efficiency for the expander, and 88% of the polytropic efficiency for the air compressors.

of this credit upon processing costs, it is assumed that the real cost of electric power generated by an expanding turbine is about 25% less than the cost of steam-generated power. At assumed projected 1980 electric rates, this reduction in power plant cost would amount to 6-1/2 mills/KWH of excess power produced by the expanding turbine-generator set. Therefore, the net credit to the process would be about 9¢/MM Btu. Obviously, this is a significant credit, but it could only be evaluated with accuracy through a detailed study.

Comparison with Economics of Previous Report

Even though the design presented in the previous report$^{(1)}$ is no longer applicable, it serves as a bench mark to determine the effect of escalation and design changes. The second column of Table III-11 depicts the system costs for the 1973 proposed design with the economics updated to reflect 1975 costs and projected escalation interest rates and operating costs to 1980. Furthermore, with the exception of the desulfurizers, 1975 ISBL installed plant cost was based on a 34.7% escalation increase from mid-1973 to mid-1975. The desulfurizers were re-estimated on the basis of 1975 cost factors. The 1973 OSBL costs were also adjusted with 1975 factors.

A comparison of the two columns clearly shows that with the exception of the increased acceptor make-up rate, the design changes proposed in this study do not markedly affect the economics of the project. On the other hand, escalation in construction and utility costs for the past two years plus higher projected interest rates and escalations of construction and utility costs for the future have increased desulfurization costs by about 63%, and account for about 70% of the total increased cost of desulfurization when compared to the economics presented in the previous report.

Economic Sensitivity Analysis

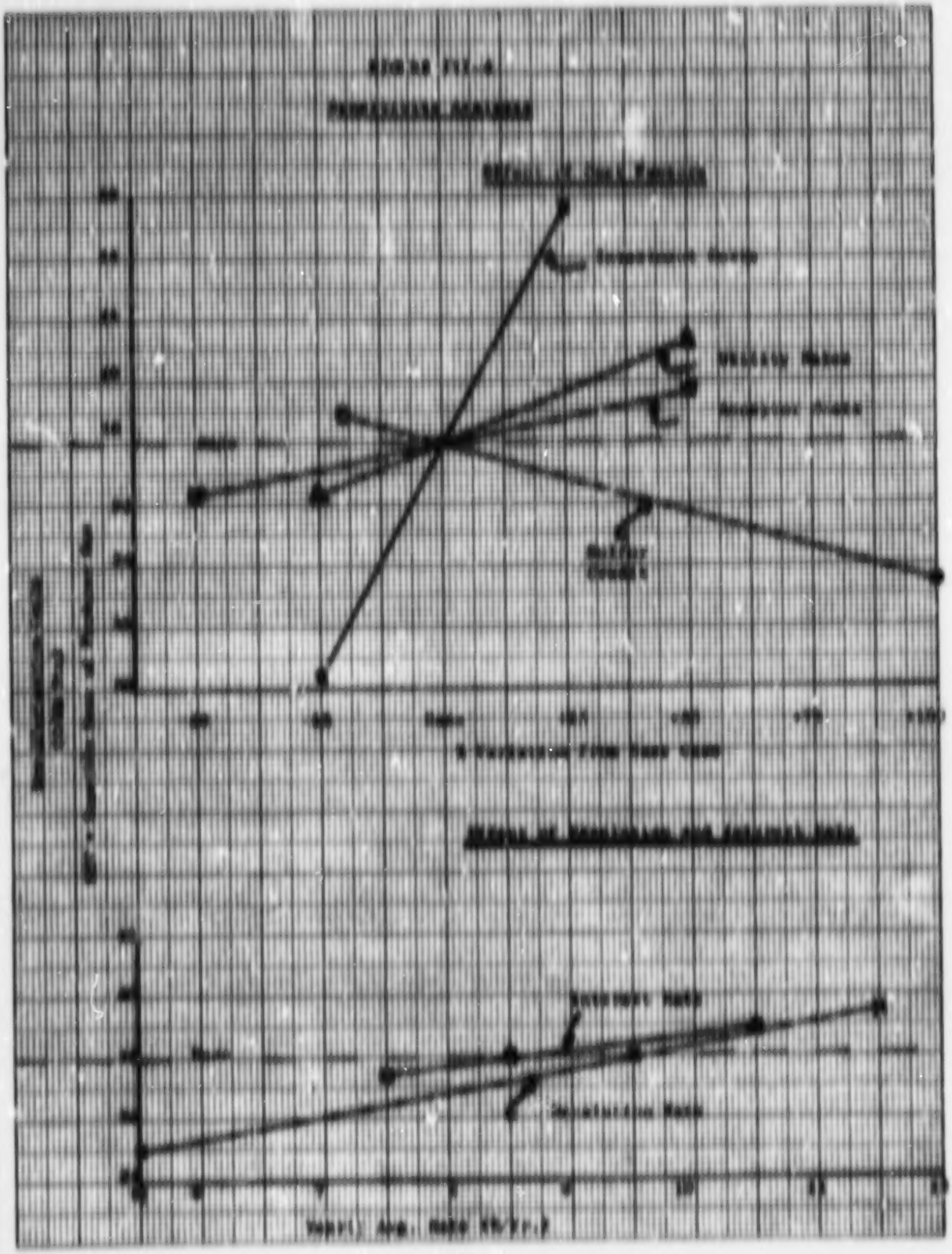
An economic sensitivity analysis was done to determine the effect of the major cost parameters on the overall process economics. The results are shown in Figure III-4 in terms of desulfurization costs of product gas including HHV and sensible heat.

The cost of desulfurization is very sensitive to investment costs. Within the accuracy limits of the estimate (± 25%), desulfurization cost of the product gas could vary from 30.4 to 45.6¢/MM Btu.

Desulfurization cost is also fairly sensitive to utility rates. Within a predictable range of 1980 utility rates, desulfurization costs could vary from 36.3 to 41.4¢/MM Btu.

The effect of the varying sulfur credit on desulfurization cost is noteworthy. Although a sulfur credit of $35/metric ton was chosen for the base case, the future sulfur market is so uncertain that sulfur value could easily range from $20 to $50/metric ton. At $50/metric ton, the sulfur credit would recover about 21% of the gross annual operating costs for desulfurization. Expressed in another way, for every $10 increase in sulfur price, the cost of desulfurization is reduced by 1-3/4¢/MM Btu.

Conversely, desulfurization cost is fairly insensitive to acceptor cost, escalation rate and interest rate within the projected ranges of those variables. For example, an acceptor cost of 150% the base would result in a desulfurization cost of only about 1.7¢ higher than the base case.



Potential Impact of Using Combined Cycle Power Station on Desulfurization Economics

It is interesting to demonstrate the potential impact of using a combined cycle power station in lieu of the conventional base case on the economics of desulfurization. The effect of net station efficiency (basis HHV coal) on installed cost of desulfurization per KW is displayed in Figure III-5. The ordinate represents desulfurization costs based on the coal feed rate presented in Table III-1. The reduction in desulfurization costs is directly proportional to the increase in net power station capacity. As an example, a combined cycle power station with a net station efficiency of 43% (HHV coal) would yield about 1675 MW at a desulfurization cost of $48.90/installed KW.

B. Artificially Hardened Sorbents

The foregoing analysis assumed that a hard, active naturally occurring dolomite was available. In the event such a stone cannot be located close to a desired plant site, it might be preferable to artificially harden a local stone to minimize transportation costs associated with the raw stone. It has been shown experimentally that soft stones can be hardened without necessarily losing activity. Once in hand, the hardened stone would behave in the process in a manner indistinguishable from that of natural, hard dolomite. The technique for hardening consists of first partially sulfiding the stone and then oxidizing it. Both of these steps are carried out at typical gas desulfurizer temperatures.

The process is illustrated schematically in Figure III-6. One of the gas desulfurizers would serve as a hardening vessel for the make-up stone. The entire stream of make-up stone is fed into the hardening desulfurizer with a stream of air via a draft tube in the middle of the vessel. Raw fuel gas is fed to the bottom and is desulfurized as the stone is sulfided. Sulfided stone is drawn into the draft tube where the CaS is partially converted to $CaSO_4$. The fuel gas associated with the stone being drawn into the draft tube is burned. At the tube outlet, $CaSO_4$ is reduced back to CaS and hardening is completed. The hardened acceptor is withdrawn and sent to the acceptor regenerator.

The reactor operates adiabatically. The heat released by the oxidation reactions is balanced by the heat required to heat and sulfide the make-up stone and to calcine its $MgCO_3$ content.

A heat and material balance for the hardening desulfurizer is given in Table III-12. The gas fed to the hardening desulfurizer represents about 9% of the total fuel gas; the amount of air added is about 0.3% of the total gas. The changes in gas composition are also barely noticeable in the overall fuel gas composition as shown in Table III-13 below. There would be no significant change in total reactor volume, the hardening desulfurizer still performs the task of H_2S removal, and the existing gas requires no further treatment. However, as the heat and material balance for hardening requires only 9% of the gas to go through the hardening desulfurizer, the other desulfurizers would be proportionately larger.

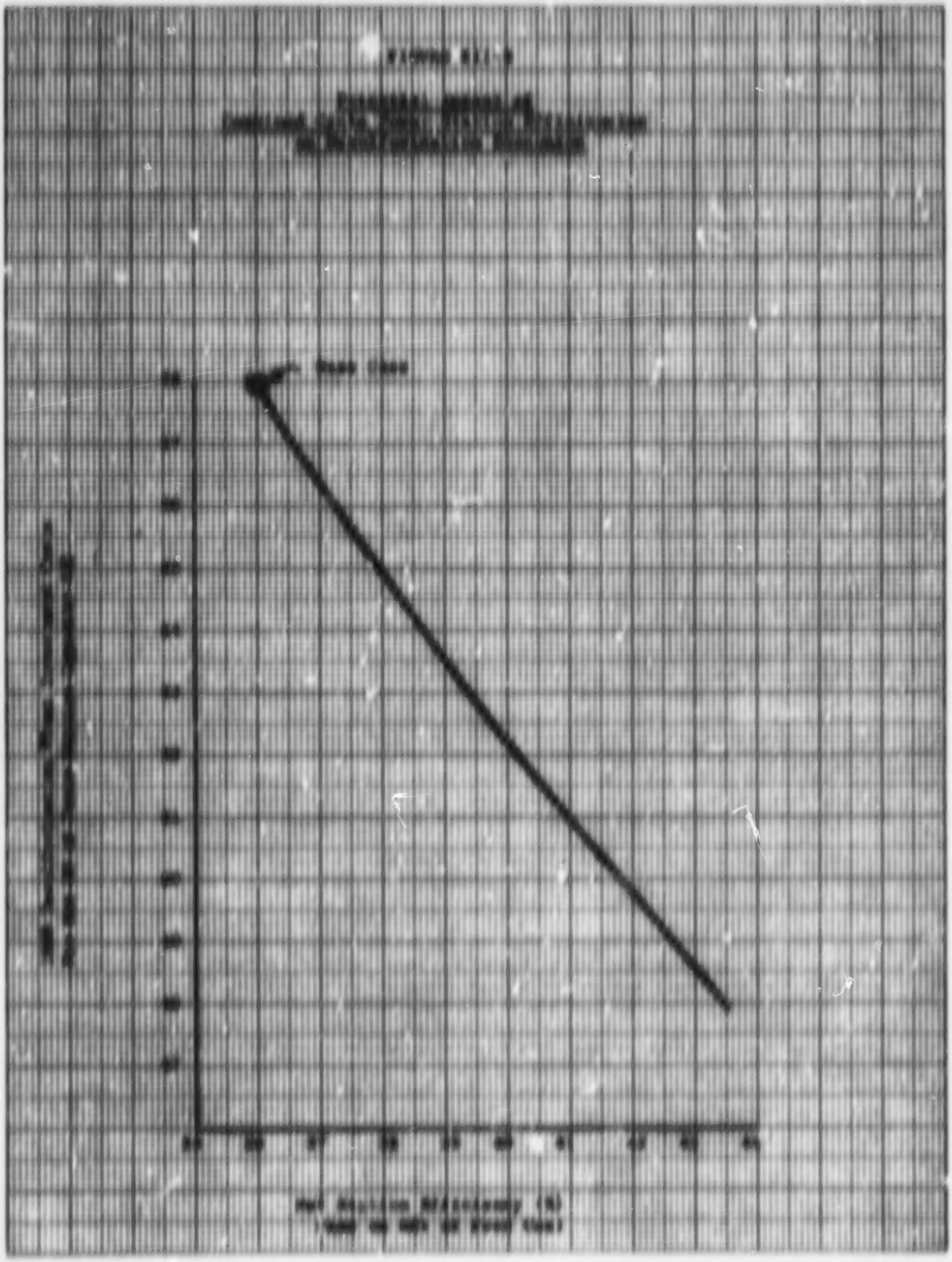
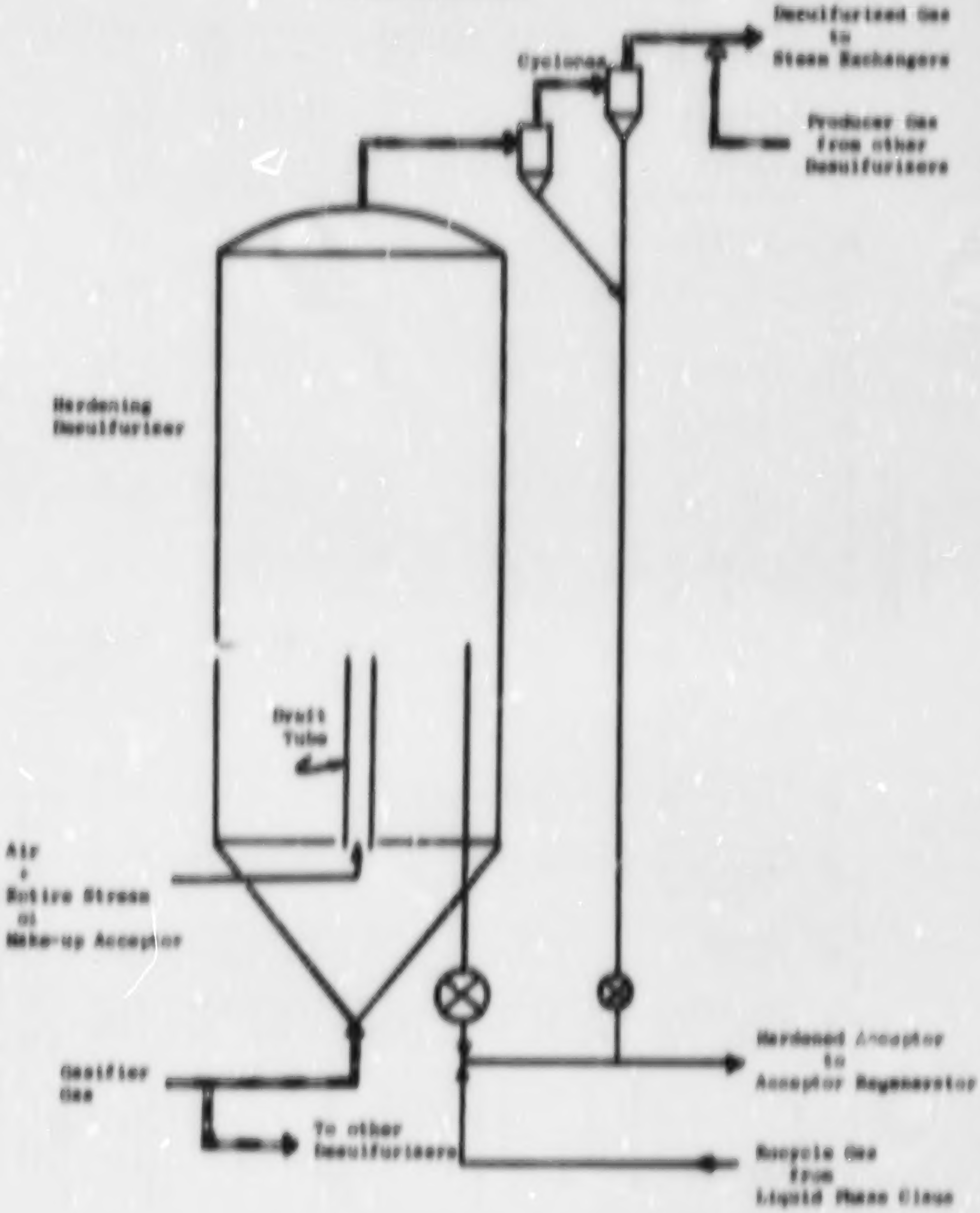


FIGURE III-6

Hardening Process


Desulfurized Gas
to
Steam Exchangers
Cyclones
Producer Gas
from other
Desulfurizers
Hardening
Desulfurizer
Draft
Tube
Air
+
Entire Stream
of
Make-up Acceptor
Gasifier
Gas
To other
Desulfurizers
Hardened Acceptor
to
Acceptor Regenerator
Recycle Gas
from
Liquid Phase Claus

Pending further experimental work on the hardening step which would include actual demonstration of hardening with a vessel containing a draft tube, there is little incentive to go to a detailed design of the system. By virtue of the reasoning given above, it is clear that no significant changes in process economics will be involved. The changes incurred by going to an artificially hardened stone are well within the accuracy of the current economic estimate.

TABLE III-12

Producer Gas Compositions With and Without Hardening

Component	Total Producer Gas Compositions Without Hardening	 With Hardening
CH_4	0.70%	0.70%
H_2	16.46	16.34
CO	16.30	16.25
CO_2	9.27	9.35
N_2	44.05	44.09
NH_3	0.23	0.23
H_2S	0.03	0.03
H_2O (v)	12.97	12.98
Total	100.00	100.00

J. Technical Uncertainties

The proposed commercial design contains a few areas of technical uncertainty. The quality of producer gas with respect to size and quantity of particulate matter and alkali that may be charged to an expander is still one area of concern. This design includes a third stage particulate collection system to remove any alkali compounds that may form at the lower gas temperatures resulting from the use of a portion of the gas sensible heat content to generate and superheat the steam required for gasification. As with the two stages of high pressure cyclones located upstream of the steam exchangers, removal efficiency is highly dependent upon the contaminants being in a discrete particle form. Furthermore, the steam exchangers are subject to fouling caused by the potential plate out of alkali compounds at the relatively low temperature tube wall conditions. One alternative is to "wet scrub" the gas as thoroughly discussed in the previous report.(1) However, water scrubbing would result in reduced power recovery from the expanding turbine-generator set and increased plant investment costs. Since preliminary experimental results have shown no traces of alkali bearing compounds in the producer gas once all the particulate matter has been removed at 1300°F, the system of "hot" cyclones plus the third stage final clean-up step was selected as the basis for this commercial design. A review of the "state of the art" in particulate removal technology at elevated temperatures is discussed in a recent report to EPRI.(7)

Another contaminant in the producer gas is ammonia. A portion of the ammonia will be converted to NO_x when burned in the power plant. The degree of conversion is unknown but, conceivably the resultant NO_x emissions could exceed "new source" standards. Results of most flame tests and furnace studies(8) indicate a low conversion of NH_3 to NO_x, i.e., less than 10%. To our knowledge, this has not been confirmed in utility steam generators. Furthermore, the ammonia concentration assumed to be present in the gas (0.23 mol percent) has not been established. It conceivably could be significantly lower in concentration. Control methods presently used to reduce NO_x emissions in gas, oil and coal-fired utility steam generators such as over fire air simulation(9) and low-excess air combustion(10) should also be applicable for burning the subject gas. If the ammonia content of the producer gas has to be reduced prior to burning in a power station, then a "wet scrub" system as discussed above would be one alternate.

There is also some technical uncertainty concerning the residence time involved with artificially hardening a dolomite stone in a draft tube of a gas desulfurizer. All experimental work to date on hardening has been done in a two-stage process with the oxidation step being accomplished in a vessel external to the desulfurization process. Even though the hardening reactions proceed rapidly, there is no experimental work to substantiate that the brief residence time inherent with the draft tube design would be sufficient to satisfy the hardening requirements. The incentive of a draft tube design compared to a dual-vessel concept are two fold: the installed costs would be less and the operability should be better. It must be re-emphasized, however, that further experimental work on the hardening step should include demonstration in a draft tube of a desulfurizer vessel.

IV. EQUIPMENT AND PROCEDURE

A. Gas Desulfurizer-Regenerator System

The gas desulfurizer-regenerator system used in this study was the same one which was described in great detail previously.(1) Figure IV-1 is the process and instrumentation diagram of the unit; the reader is referred to the previous report in this series for a detailed account of the equipment and its auxiliaries. Only changes in the system are detailed below.

In order to make the system more reliable, the hot filter system which removes attrited acceptor fines from the desulfurizer product gas was modified. Ball valves which can be closed in the presence of solids replaced the gate valves which tended to become impacted with fines making it impossible to switch filters. This had been the cause of several shutdowns. The new valves were for severe service and had hardened ball stem tips.

After Run A132, the gas desulfurizer reactor was replaced with one made from aluminized ("Alonized") 310 ss. The process of aluminizing consists of heating the equipment in a bed of fine aluminum and alumina powder. The aluminum diffuses into the steel and, after further heat treatment, is converted to an outer layer of aluminum oxide which is purported to be more resistant to H_2S corrosion than the original steel. The aluminized reactor was not in place long enough to allow a final verdict on its performance. It is noted that the aluminizing process made the vessel brittle and difficult to either weld or machine.

H_2S Analyzer

An ultraviolet continuous H_2S analyzer was purchased to monitor both vessels. The unit was a DuPont series 400 analyzer equipped with scales of 0-10 and 0-2% H_2S. Performance was generally satisfactory, but there was a continued tendency for the baseline to shift apparently due to deposition of sulfur on the cell lenses.

CS_2 Supply System

The original liquid H_2S feed system was replaced with a CS_2 feed system.

Some of the various reasons for the substitution were as follows:

1. The steel cylinders in which H_2S was delivered contained not only H_2S but also products of corrosion, oil, water, noncondensable gases and organic compounds of sulfur. An attempt to distill H_2S into new, clean steel cylinders failed because of the presence of noncondensable gases.

2. Even a micron porometallic filter in the supply line from cylinders to the metering pump did not prevent solid matter from entering the chamber of the pump. Solid matter deposited in the check valves of the pump resulting in an erratic, unreliable delivery of liquid H_2S.

3. At the H_2S flashing point, the sudden drop in temperature caused water in the liquid H_2S to freeze and soluble matter to deposit and plug the feed line.

Tests for decomposition of the CS_2 vapor at the desulfurizer reactor conditions have shown a satisfactory hydrolysis of CS_2 in the presence of H_2, H_2O and CO_2 in the inlet gas. When no hydrogen was fed into the desulfurizer reactor, a small amount of solid carbon was found in the sulfur acceptor and in the gas preheater tubing.

A schematic of the CS_2 feed system is shown in Figure IV-2. Liquid CS_2 was kept under a thin layer of water in a glass graduated holder. CS_2 withdrawal from the holder was metered via a Lapp Model LS-20 diaphragm pump with a jacketed head maintained at 4°C (40°F) to prevent variations in the specific volume of liquid CS_2 and vapor lock.

Hourly readings of the liquid CS_2 level in the reservoir were used for an observation of the metering pump performance.

The calibration of the pump has shown an accuracy within ± 1% of a feed rate, the variance being due to the pump double ball check valve slippage.

Liquid CS_2 was fed into the gas mixing manifold most of the time. However, when the steam generator had to be used, the CS_2 feed line was connected to the saturator exit line to prevent CS_2 hydrolysis in the saturator.

B. Hardness Testing

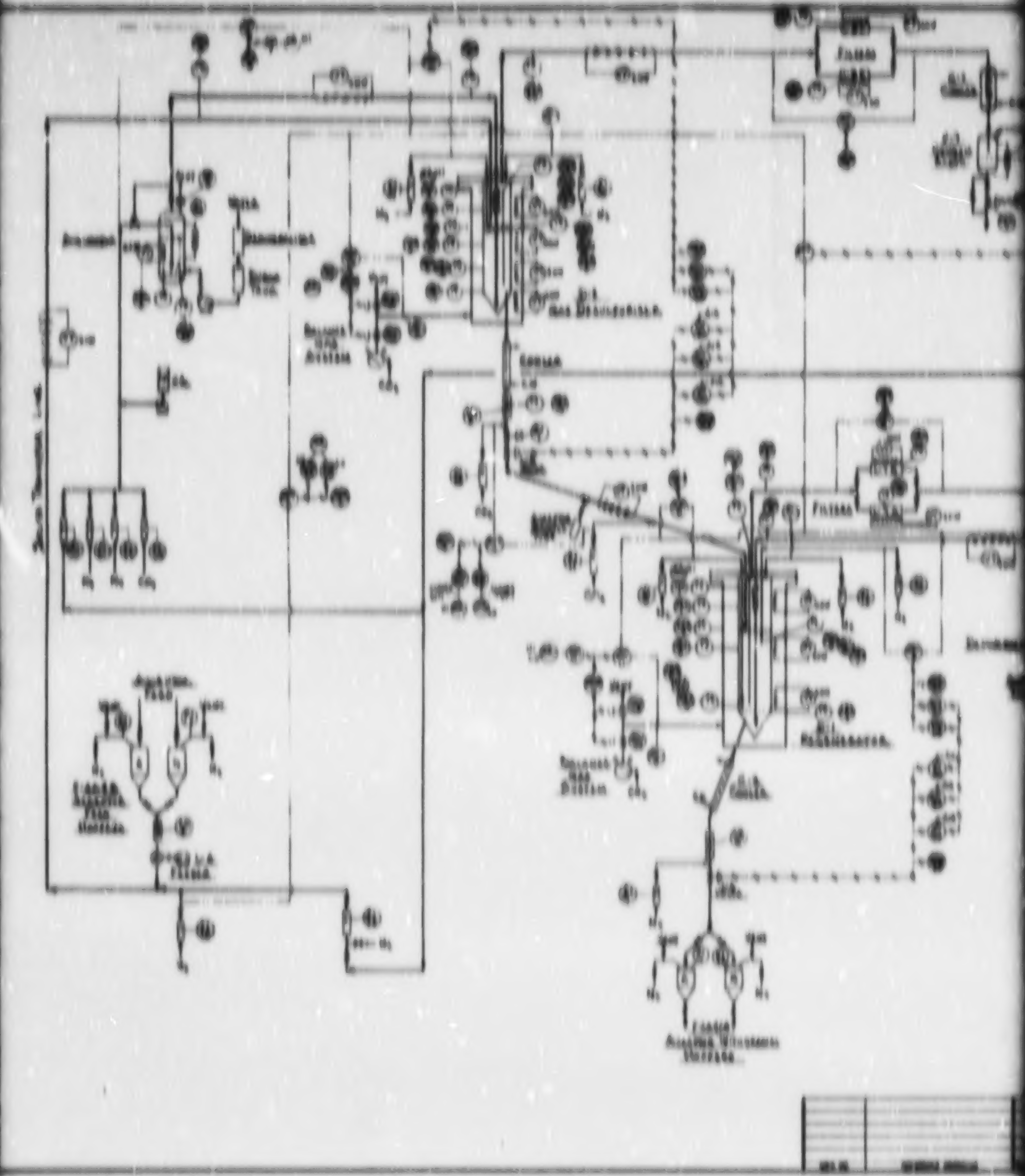
Two techniques were used to check the attrition resistance of stones on a laboratory scale. The first was a rolling mill test. About 100 grams of material to be tested was placed in a Roalox tumbling jar together with ten size 00 Burundum grinding cylinders (13/16" x 13/16"). The jar was tumbled in a rolling mill for 30 minutes at 51 rpm. The sample was then screened, and the external surface area calculated from its size distribution. The hardness was the increase in surface area which occurred due to the test divided by the increase observed for a standard hard stone. The standard was A8 product, a Tymochtee dolomite which had been hardened in the CO_2 Acceptor Process, which displayed an increment in surface area of 220 cm²/gm.

The second method was to perform a drop test with the apparatus shown in Figure IV-3. A sample of test stone was screened before and after a metal rod crushed it in a small holder. This latter test was abandoned in favor of the rolling mill test as the rolling mill test gave results more in agreement with the stone's actual attrition resistance in the fluidized bed system.

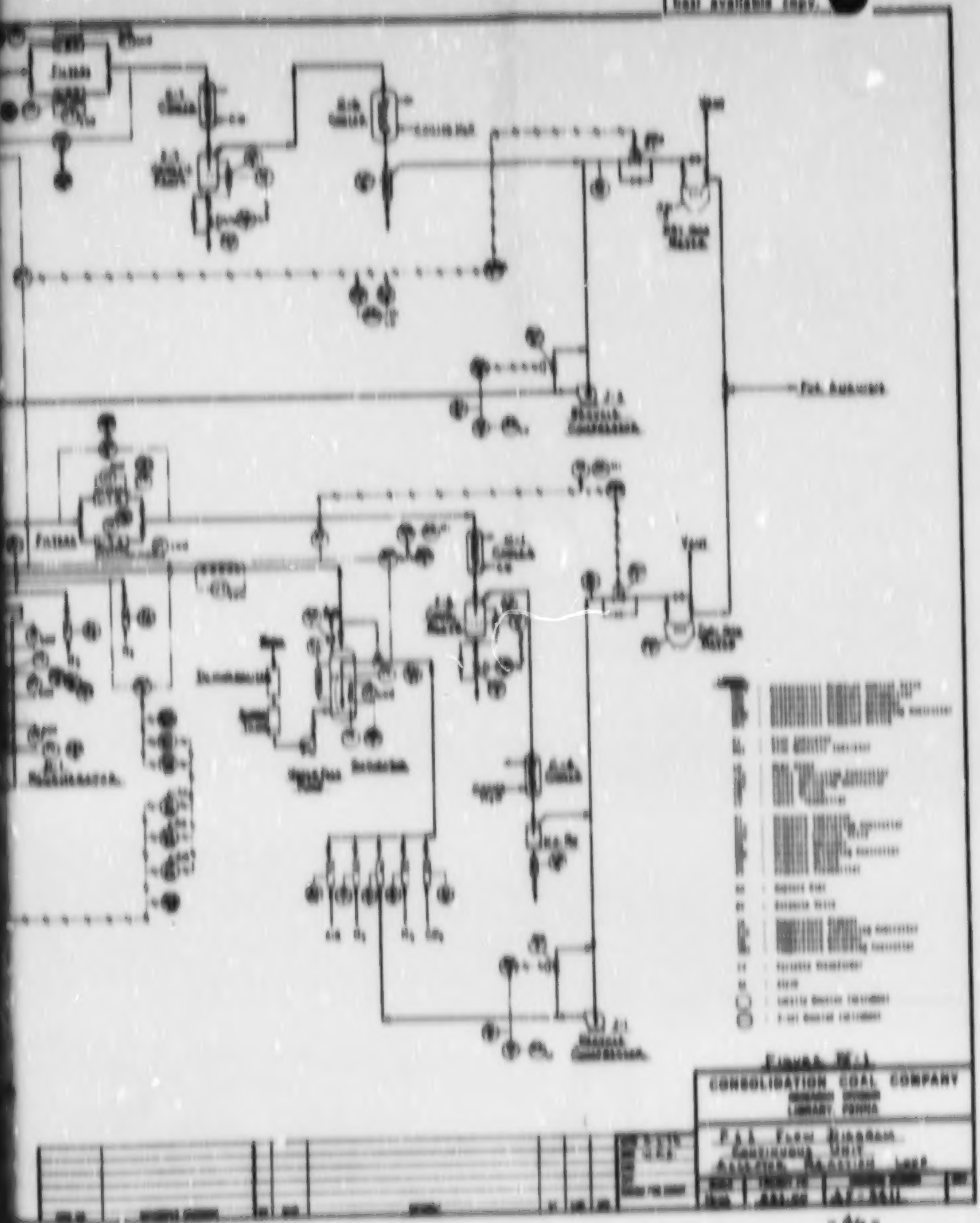
C. Fine $CaCO_3$ Runs

A simplified flow diagram for a trial run using Fisher precipitated calcium carbonate in a water slurry is shown in Figure IV-4.

The regenerator vessel (D-1) was converted into a solids trap by installing two star shaped porometallic filter elements. The solids receiving space was maintained at 343°C (650°F) for "freezing" all downstream reactions yet preventing water vapor condensation.

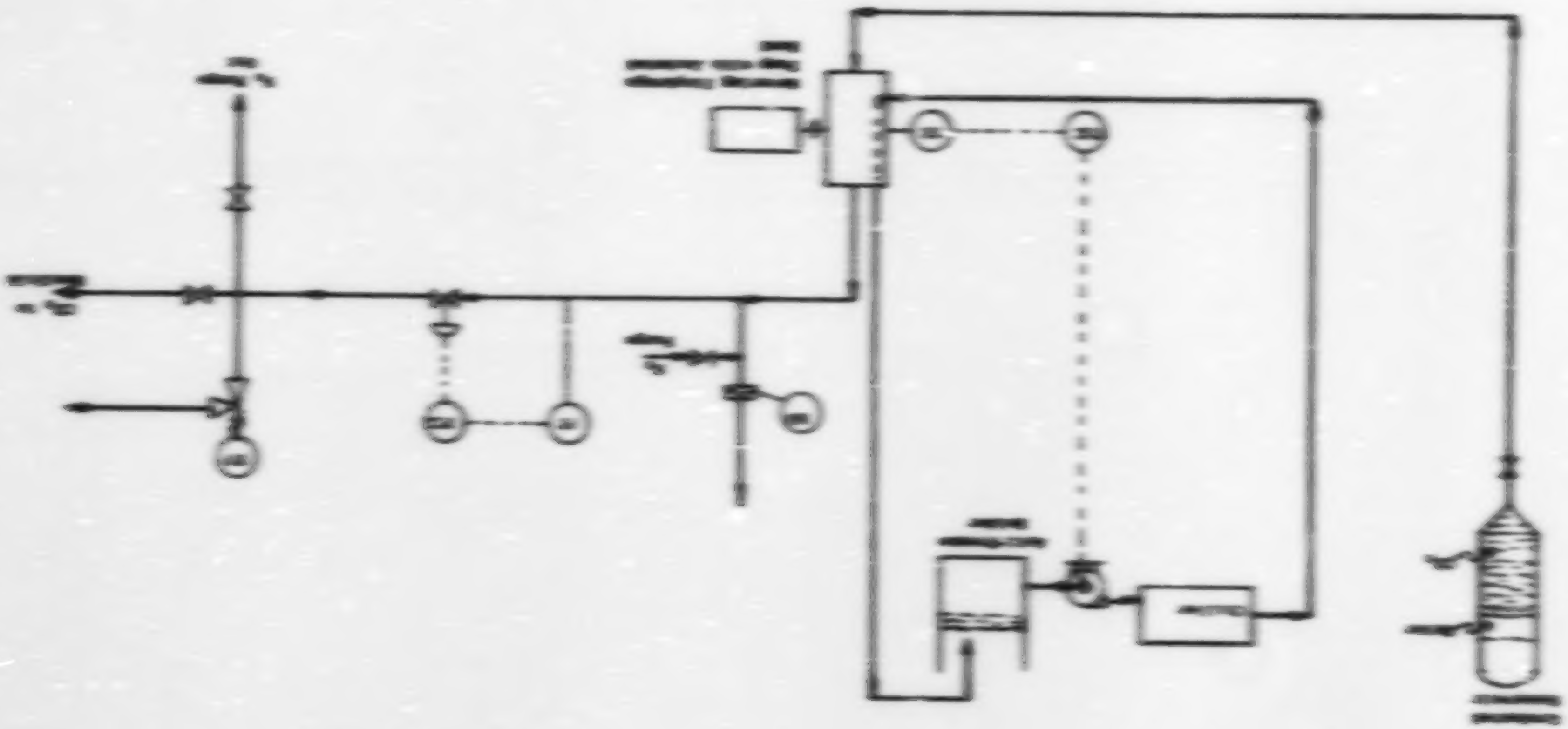


Reproduced from best available copy.



Vent
Vent
Fd. Analysis
Coolant
N₂
CO₂
CONSOLIDATION COAL COMPANY
RESEARCH DIVISION
LIBRARY, PENNA
P & I Flow Diagram
Continuous Unit
Acceptor Reaction Loop

Figure III-1



[illegible]

[illegible]

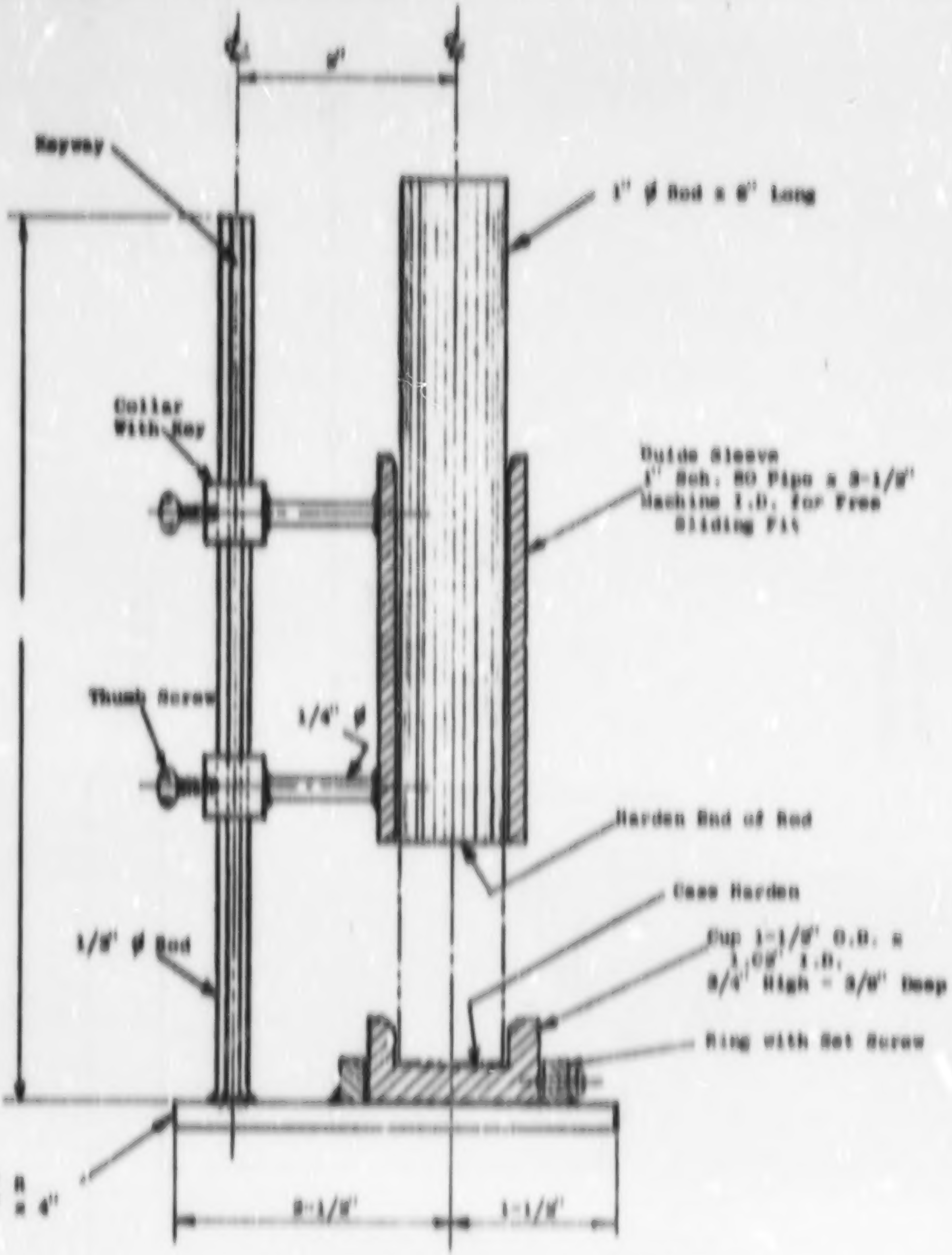

3"
Keyway
1" ø Rod x 6" Long
Collar With Key
Guide Sleeve
1" Sch. 80 Pipe x 3-1/2"
Machine I.D. for Free
Sliding Fit
Thumb Screw
1/4" ø
Harden End of Rod
Case Harden
1/2" ø Rod
Cup 1-1/8" O.D. x
1.03" I.D.
3/4" High - 3/8" Deep
Ring with Set Screw
1/2" R
4" x 4"
2-1/2"
1-1/2"

FIGURE IV-3

Drop Tester for Acceptor Hardness - Dwg. DN-2481

Project No. 555.08 10/18/73

The chalk slurry feed system consisted of a continuously stirred tank filled with water and $CaCO_3$ to give a ratio of 35 wt % solids in the slurry. A Lapp metering double ball check valve diaphragm pump provided slurry transportation.

Inert bed material was fed into the desulfurizer (D-2) vessel through the L-4 feeder. Both coating of the ball checks with chalk and segregation of slurry in the check valves of the pump prevented satisfactory performance of the apparatus.

A simplified flow diagram for a trial run using Fisher's precipitated calcium carbonate in a dry form is shown in Figure IV-5.

Tablets prepared by pressing calcium carbonate with 10 wt % of water were dried, crushed and screened to 20 x 48 mesh size. However, the feedstock was so soft it did not survive shearing forces between the rotor and the body of the L-4 feeder which ground lumps of chalk into powder. The pockets of the rotor gradually became filled thus preventing a uniform feed rate.

A compromise run to test use of calcium carbonate for desulfurization was made with Nebraska limestone. Since the L-4 rotary feeder could not reliably feed powdery material, a series of tests was performed in order to find a size consist as fine as possible so the rates of the calcination and desulfurization reactions would be limited as little as possible. At the same time, the finely divided feedstock had to be fed at a uniform rate. Run L-1 was made with 65 x 150 mesh Nebraska limestone and, after polishing the rotor and body of the feeder, 150 x 200 mesh stone was used for Run L-2.

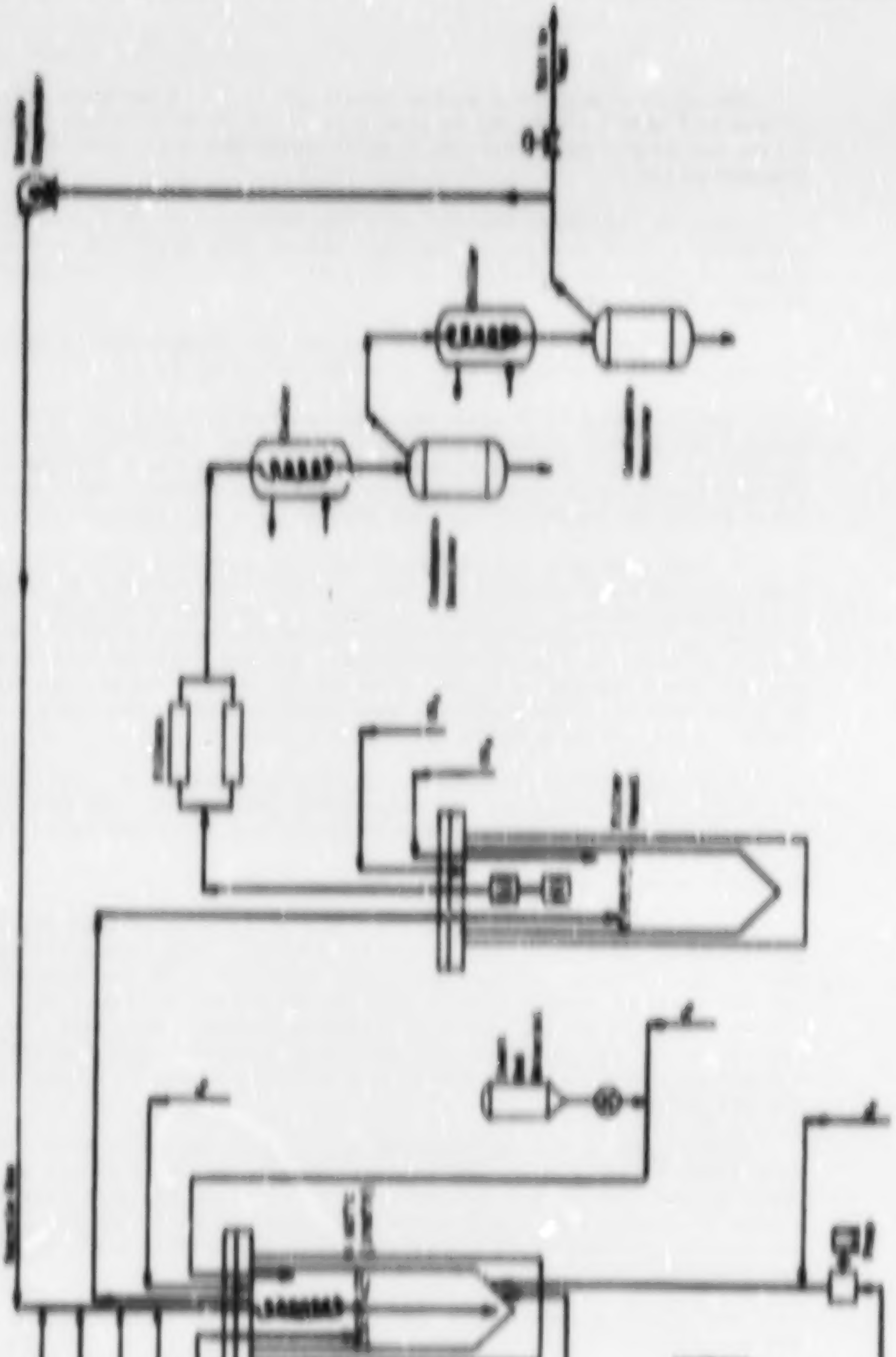
A bed of dead-burned dolomite was established in the desulfurizer vessel for Run L-1 and, after the bed temperature leveled out, the CO_2 and limestone feed systems were turned on. Magnorite was the inert bed material in Run L-2.

D. Hot Removal of Particulates and Alkali Fume

Figure IV-6 shows the flow diagram for the runs to test the removal of particulates and alkali fume at 704°C (1300°F). Fluidizing gas and solids were fed to the bottom of the gas desulfurizer vessel. The gas containing alkali and particulates passed through the bed and exited through a heated line to a filter vessel contained inside a heated enclosure. The filter vessel and heated enclosure, called a hot box, are detailed in Figures IV-7 and IV-8. The system was set up so that the gas would be maintained at 704°C or above until is passed through the filter.

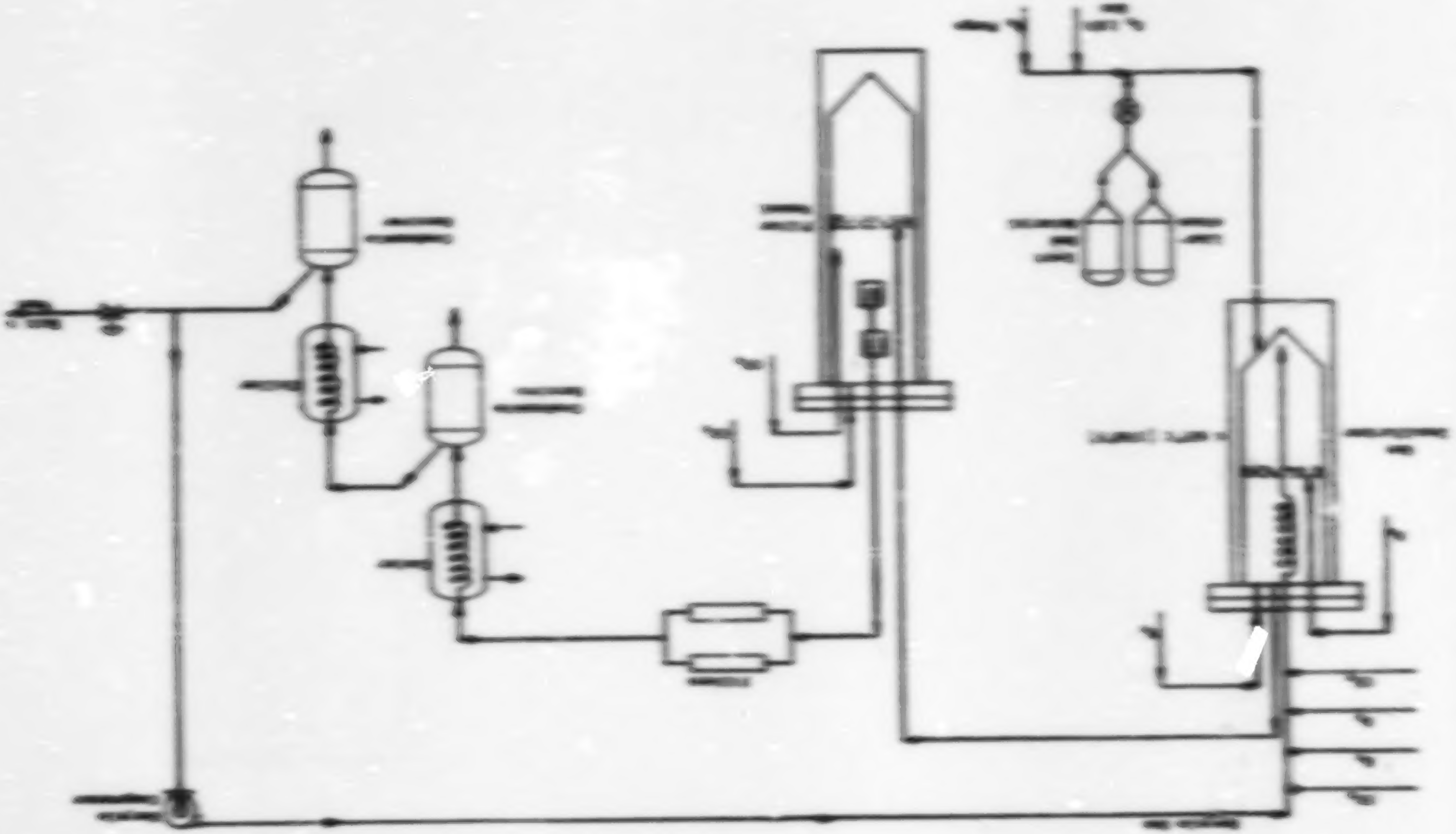
The flange of the desulfurizer was a large source of heat loss. When steps were taken to apply extra heat to the flange, the brass gasket on the outer shell leaked. The brass was replaced with a stainless steel and asbestos composite ("Flexitallic" brand) which gave improved performance. The flange was ultimately operated at 621°C (1150°F) with a tolerably small leakage rate of balance gas.

The filter vessel itself was constructed from a gas sampling cylinder which was cut open so that a 20 micron opening stainless steel sintered porous plate filter could be welded into place. All piping materials were 316 ss. Piping inside the hot box consisted of schedule 80 or 160 pipe or Autoclave Engineers' medium to high pressure tubing welded to 6000 psi fittings. The line from the reactor to the hot box was schedule 160 ss pipe. All connections were welded except for a Grayloc union at the gas desulfurizer outlet.



[illegible]

[illegible]



[illegible]

[illegible]

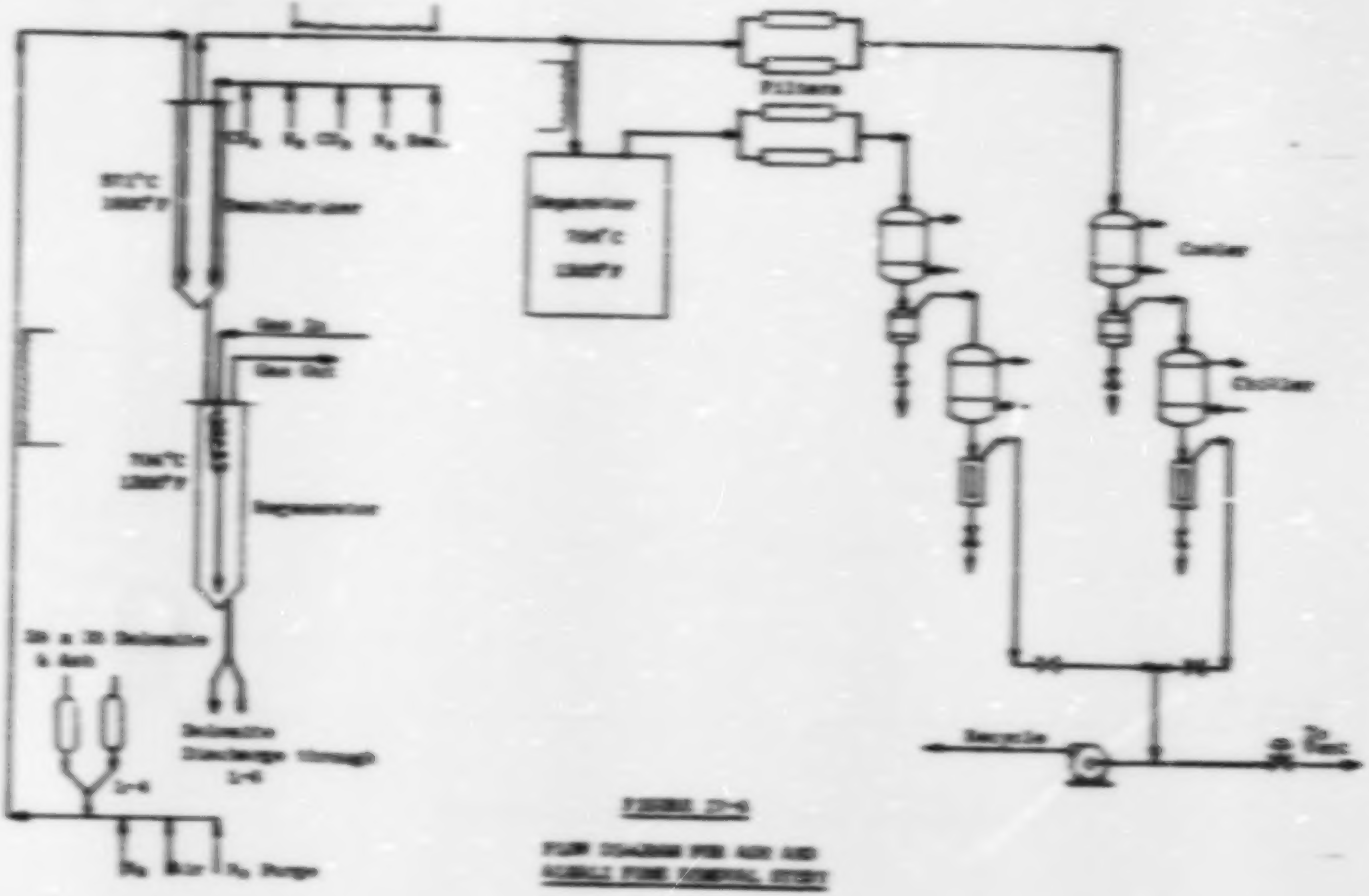
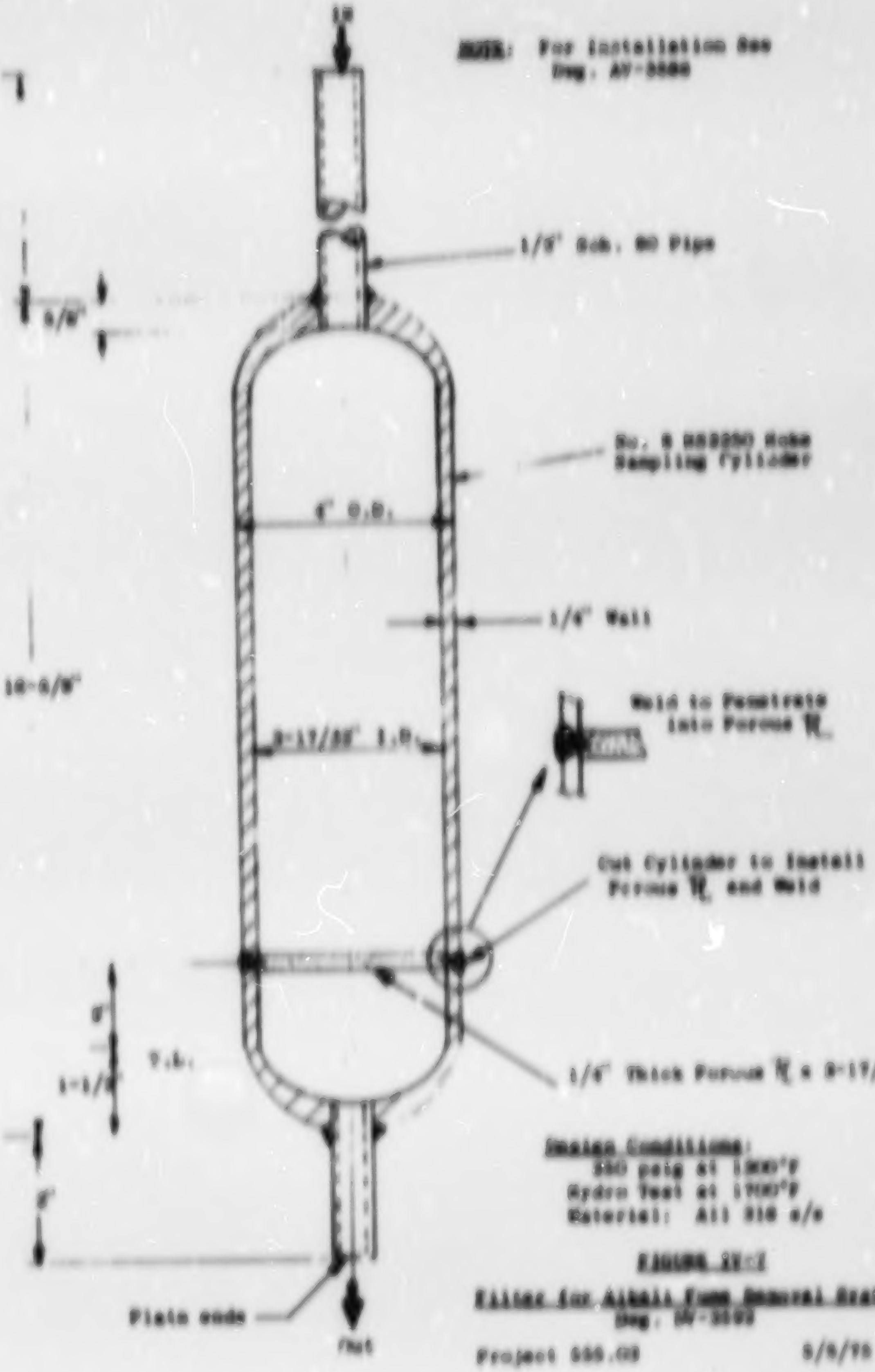

Filters
871°C
1600°F
Gasifier
CH_4 H_2 CO_2 N_2 Steam
Regenerator
704°C
1300°F
Gas In
Gas Out
704°C
1300°F
Regenerator
Cooler
Chiller
Dolomite
Discharge through
L-V
L-V
N_2 Air N_2 Purge
Recycle
To Vent

FIGURE 2-6

FLOW DIAGRAM FOR ASH AND
ALKALI FUME REMOVAL STUDY

NOTE: For Installation See Dwg. AY-5080

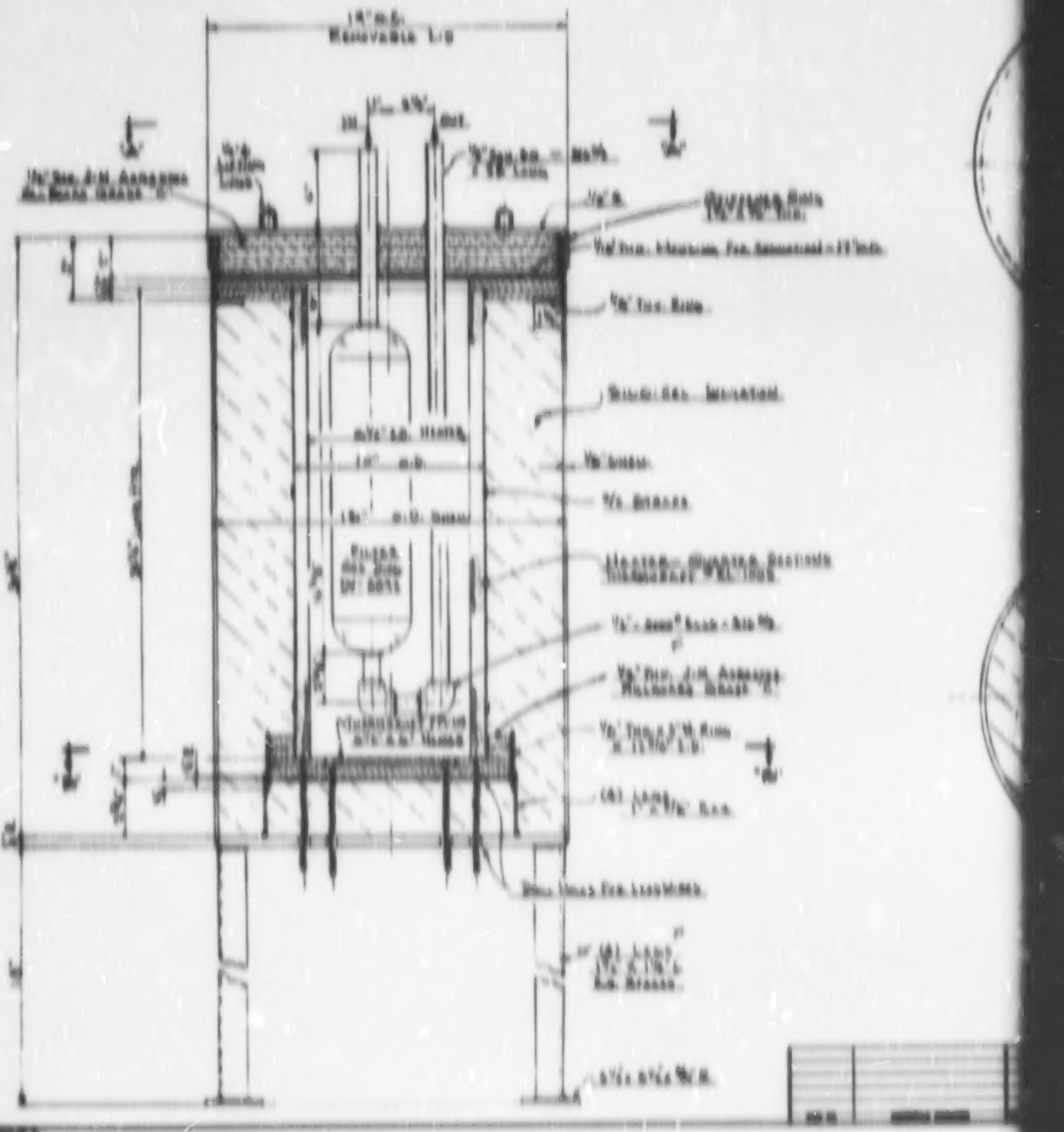

In
1/2" Sch. 80 Pipe
5/8"
No. 8 HS8250 Hoke Sampling Cylinder
4" O.D.
1/4" Wall
10-5/8"
Weld to Penetrate into Porous PL
3-17/32" I.D.
Cut Cylinder to Install Porous PL and Weld
3"
T.L.
1-1/2"
1/4" Thick Porous PL x 3-17/32"
6"
Plain ends
Out

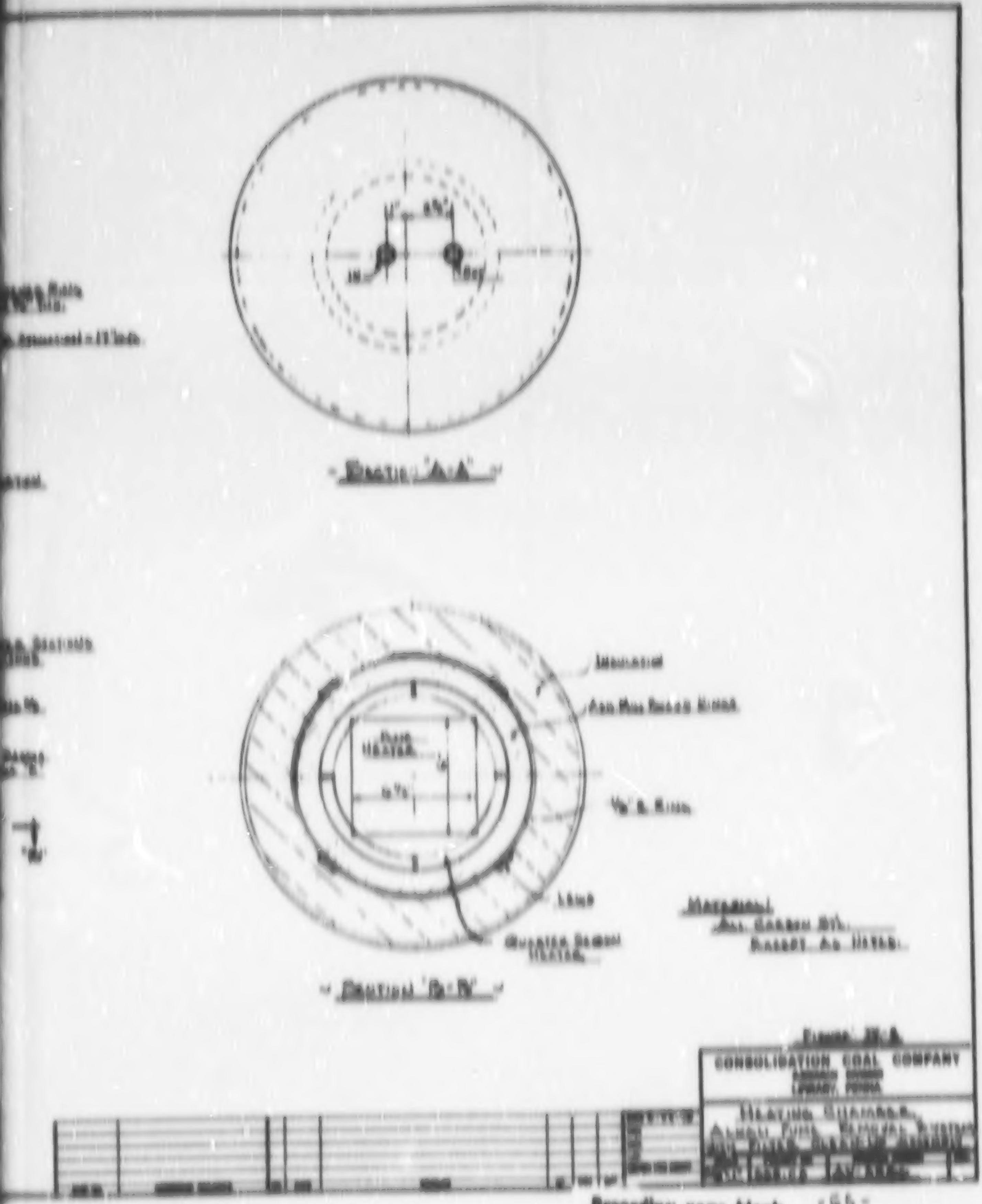
Design Conditions:
350 psig at 1300°F
Hydro Test at 1700°F
Material: All 316 s/s

FIGURE IV-7

Filter for Alkali Fume Removal System
Dwg. SK-3302

Project 555.03 5/6/75


Removable Lid
In
Out


Section 'A-A'
Section 'B-B'
Insulation
Material:
All Carbon Stl.
Except As Noted.
CONSOLIDATION COAL COMPANY

Preceding page blank

The hot portion of the system was extensively instrumented and fitted with alarms so that the temperature could be closely monitored.

Due to concern about possible contamination of equipment by alkali generated during start up of a run, an entirely separate condensate system was appended to the unit. When gas was switched to the hot filter, it exited through a second set of 800°C filters and a second condensate system.

The procedure was to startup as if an ordinary run were to be made. The circulation of acceptor was continued for several cycles to build up the level of sulfur in the stone and to allow any volatiles to be purged from the dolomite. To start feeding fines and alkali, the withdrawn acceptor was collected in a surge container and 1000 grams were mixed with the additive material. This was then placed into the feed hopper. Several minutes after that hopper was started, the exit gas flow was switched to the filter and alternate condensate system.

Upon completion of the run, the lines were taken apart and flushed with dilute nitric acid to remove any alkali from the walls. Fines were removed from the filter by backflushing with air.

E. Chance Reaction

The liquid-phase Chance reaction,

$$CaS_{(s)} + CO_{2(g)} + H_2O_{(l)} \rightarrow CaCO_{3(s)} + H_2S_{(g)}$$

was studied batchwise in a glass laboratory apparatus at atmospheric pressure. The reactor was a 500 ml standard resin reaction flask. For runs at elevated temperatures, heat was supplied by heating a mantle. The flask cover was provided with joints for a sampling device, a thermometer, a gas inlet, a stirrer and a gas outlet through a reflux condenser.

In a typical run, the assembled apparatus was charged with a batch of 400 ml of distilled water and 25 grams of acceptor. The run was started after air was purged from the apparatus by N_2 and the temperature leveled off.

Hydrosulfidation was carried out with 100% H_2S until there were no visible changes in the slurry color and texture. The reaction was always completed in less than one-half hour. Pure CO_2 was used for carbonation, and the run continued until no H_2S could be detected in the offgas. After switching to the reactive gas mix, the course of the reaction was followed by analyzing the exit gas composition and the sulfur content of the acceptor-water slurry. The run was terminated by purging out CO_2 and cooling down the slurry. This was followed by filtration and analysis of the dry cake for sulfur.

Exit gas was analyzed for CO_2 and H_2S by a calibrated gas chromatograph. Samples of gases were taken at 15-minute intervals. Slurry and solids samples were analyzed for sulfide sulfur content by decomposition in an acidified iodine solution followed by titration with thiosulfate. Product solids were filtered at ambient temperature and dried in a vacuum oven overnight prior to analysis.

F. Lab-Scale Batch Acceptor Cycling Reactor

An assembly drawing of the reactor is shown in Figure IV-9. The unit was arranged for pressure balanced operation. The furnaces and the one-inch reactor were contained in a 3-1/2" ID autoclave shell. Heat was supplied by two windings of 18 gauge Kanthal A-1 wire on an Alundum core. The full gas flow was maintained at all times. Synthesized fuel gas entered through the top, and the regenerator feed entered through the bottom. The gas streams merged between the reaction zones and exited through the annulus connected to the bottom.

The acceptor sample was held in a ceramic basket suspended from a centered piece of 1/4" tubing. Originally a platinum mesh basket was used, but it fell apart under the severe operating conditions in our system. This was believed to be due to the formation of platinum carbide and/or solutions of carbon in platinum which form under reducing conditions and which are extremely brittle. Cycling was effected by moving the central tubing up and down through a packing gland above the head. A thermocouple embedded in the acceptor sample measured the temperature.

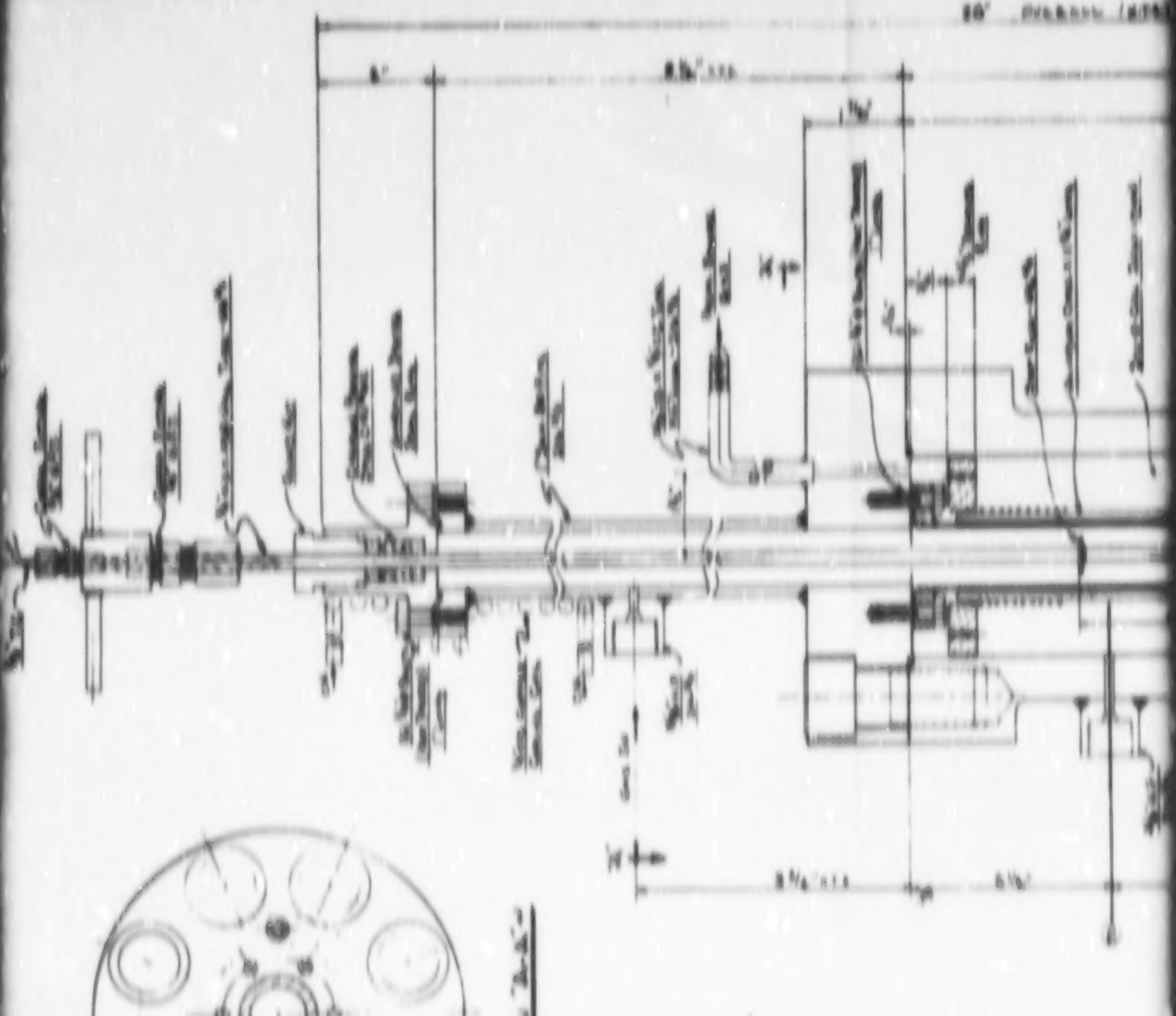
A flow diagram of the system is given in Figure IV-10. Gas is metered in via two sets of rotameters. Flow to the bottom section can be switched to a saturator to provide the required steam. However, in order to simplify the feed system, the required H_2O feed to the upper reaction zone was made via the water-gas-shift reaction. Gas chromatograph and condensate measurements confirmed that shift equilibrium was closely approached.

Temperature profiles were taken which showed that the desired temperatures of 1600 and 1300°F (871 and 704°C) could be maintained in the two separate heating zones.

Since two separate reactions were involved, diffusional mixing (interpenetration) of the two feed gases was to be avoided. Interpenetration was studied by substituting a 1/8" tube for the sample thermocouple and taking a small gas flow to a thermal conductivity cell. Nitrogen was passed through the reference cell and the sample gas through the second balanced cell. Nitrogen was fed over the sample gas part, and 50% H_2-N_2 through the opposing reaction zone. The observed response was less than 1% of the response due to the H_2-N_2 mixture indicating that the sampled gas was nearly pure nitrogen.

The operating procedure was to place a weighed sample of acceptor in the mesh basket, and then withdraw the "support" tube until the stop hit the packing gland. The entire upper assembly was then lowered into the assembled autoclave and the upper flange bolted tight. In this position, the sample sat in the "cold" part of the reactor above the autoclave flange. The unit was then pressured up and brought to the programmed Powerstat settings. As a rule, the system was kept hot at all times.

The run was started by immersing the sample into the upper, or gas desulfurizer, zone for half-calcining and sulfidation at the programmed conditions of time, temperature and gas composition. The sample was then lowered into the regenerator zone to complete a cycle. The procedure was repeated until the desired number of cycles was completed. The run was ended by withdrawing the sample from the regenerator zone into the cool zone above the autoclave flange. Throughout the entire run, the sample temperature was recorded continuously.

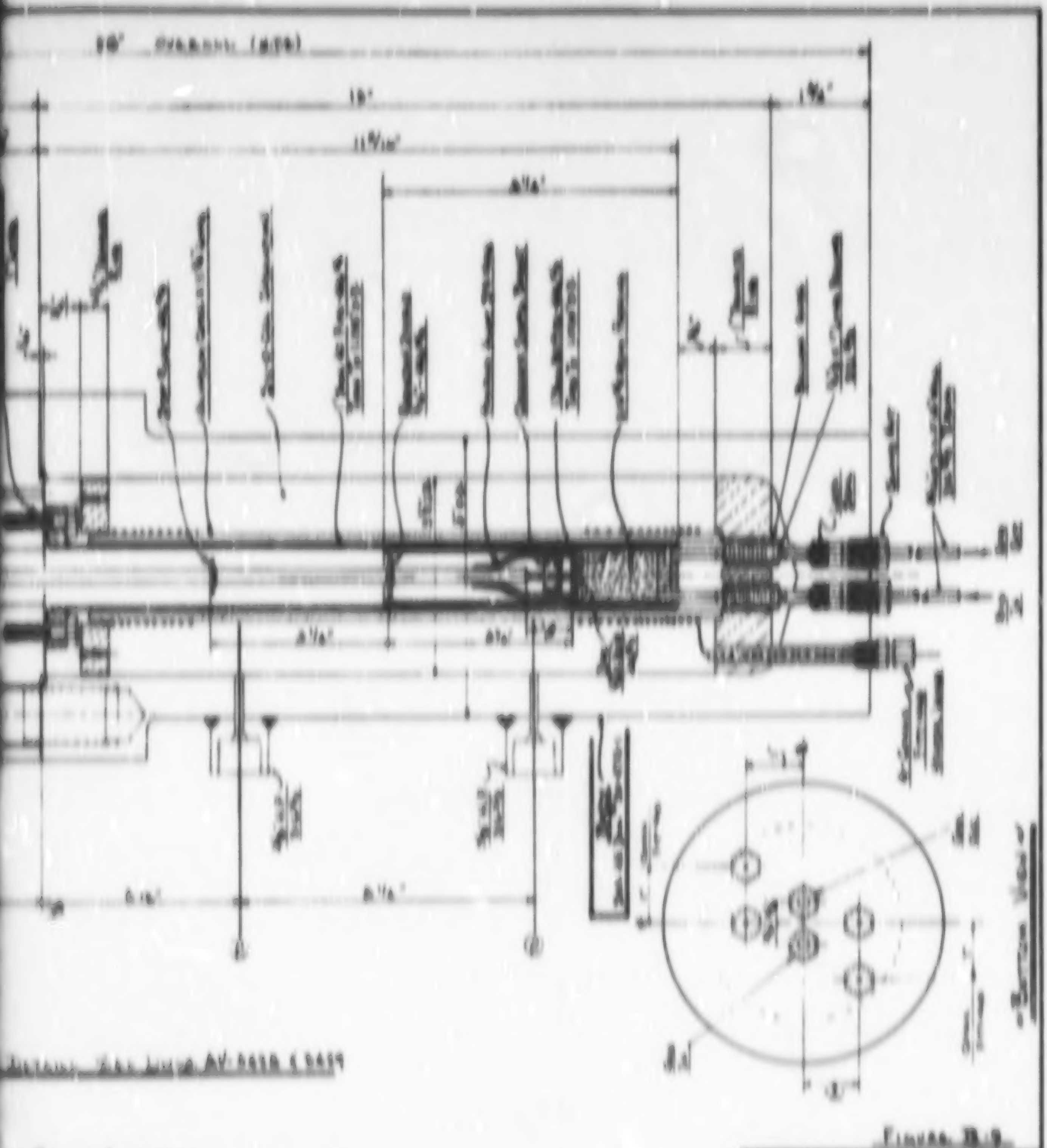


Notes.

For Details See Dwg AV-5858

Design Conditions

[illegible]


30" Overall (Ref)
15"
1 3/4"
11 9/16"
8 1/4"
8 1/8"
A
B
Bottom View

Details: See Dwgs AV-5958 & 5959

Design Conditions: 800 PSIG @ 1000°F Max.

Figure B-9

CONSOLIDATION COAL COMPANY
RESEARCH DIVISION
LIBRARY, PENNA

Reactor Assembly
Low Press. Reactor, Ground Station

The unit was depressured and the acceptor removed by taking out the entire support rod assembly. The sample was removed from the basket and weighed to determine the CaS content.

G. Reduction of $CaSO_4$ by H_2S

The unit arrangement for reduction of $CaSO_4$ by H_2S was the same as for desulfurization-regeneration runs.

The only changes made were on the vapor condensing system of the unit to deal with elemental sulfur vapor in addition to water vapor. The condensing system using cooling water only did not perform satisfactorily due to plugging of the heat exchanger gas side by solid sulfur.

The substitution of steam for cooling water in the first stage of condensing system No. 1 as shown in Figure IV-11 was only partially successful. In this arrangement high viscosity elemental sulfur condensed on the gas side of the heat exchanger coil and prevented smooth operation of the condensing system.

A satisfactory solution to the problem was reached by arranging the equipment as shown in Figure IV-12. Most of the elemental sulfur was trapped as liquid in the high temperature condenser-receiver vessel. Only minute amounts of elemental sulfur ended up in the cold parts of the condensing system.

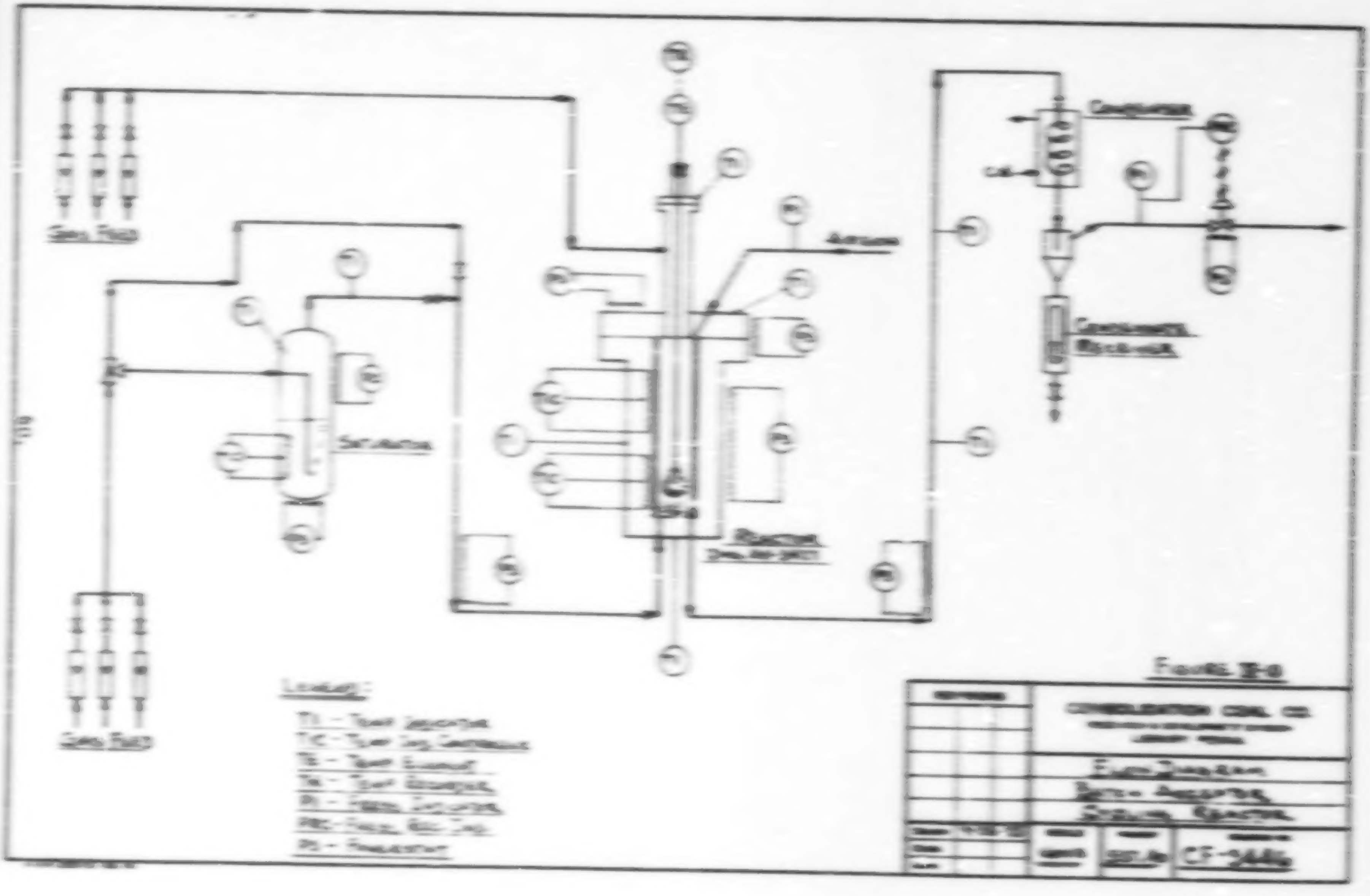

Gas Feed
Gas Feed
Saturator
Reactor
Condenser
Condensate Receiver
Legend:
TI - Temp Indicator
TIC - Temp Ind. Controller
TE - Temp Element
TR - Temp Recorder
PI - Press. Indicator
PRC - Press. Rec. Cont.
PS - Pressurestat
Figure III-8
Consolidation Coal Co.
Flow Diagram
CF-2446

FIGURE IV-11

SULFUR CONDENSING SYSTEM NO. 1

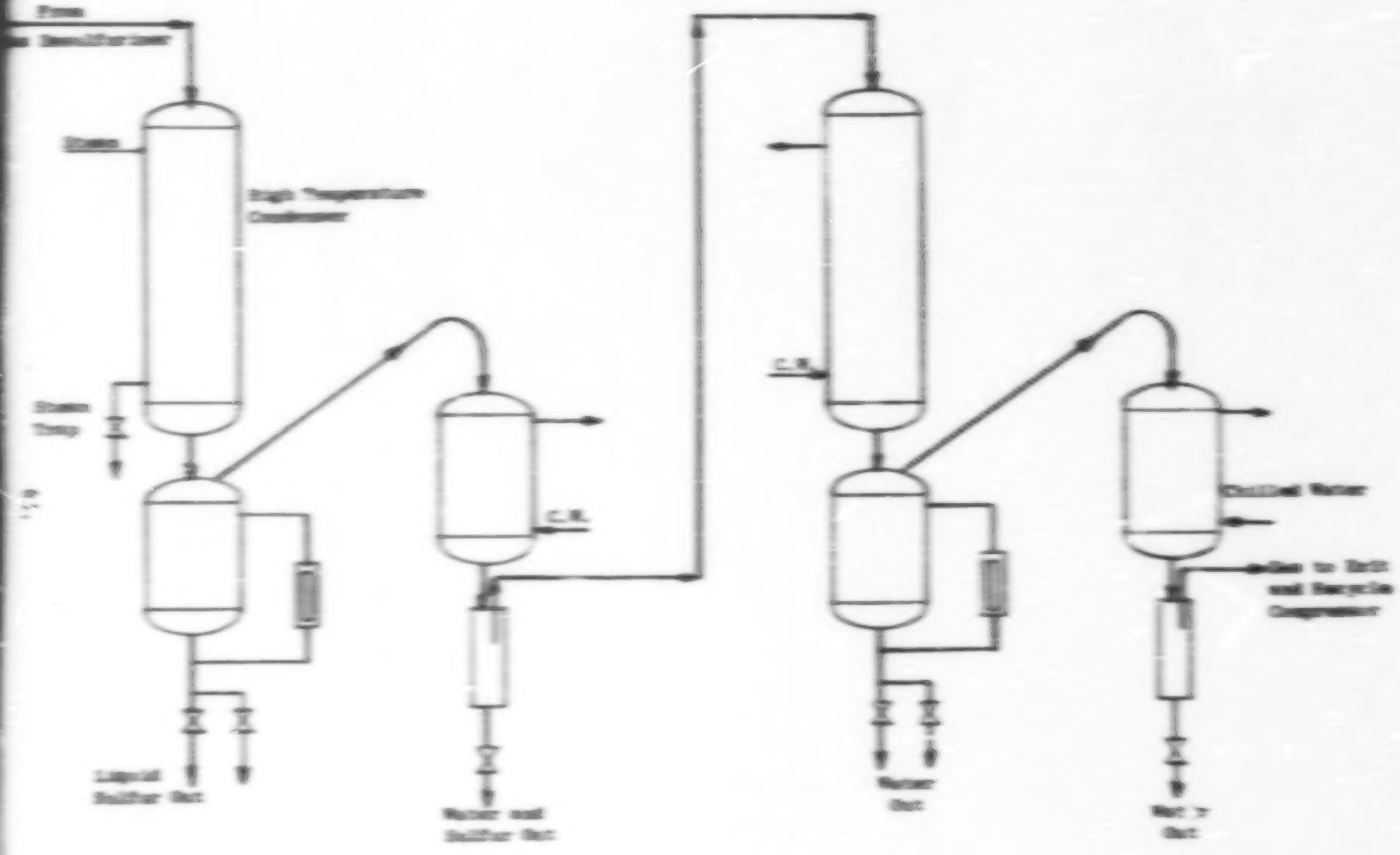
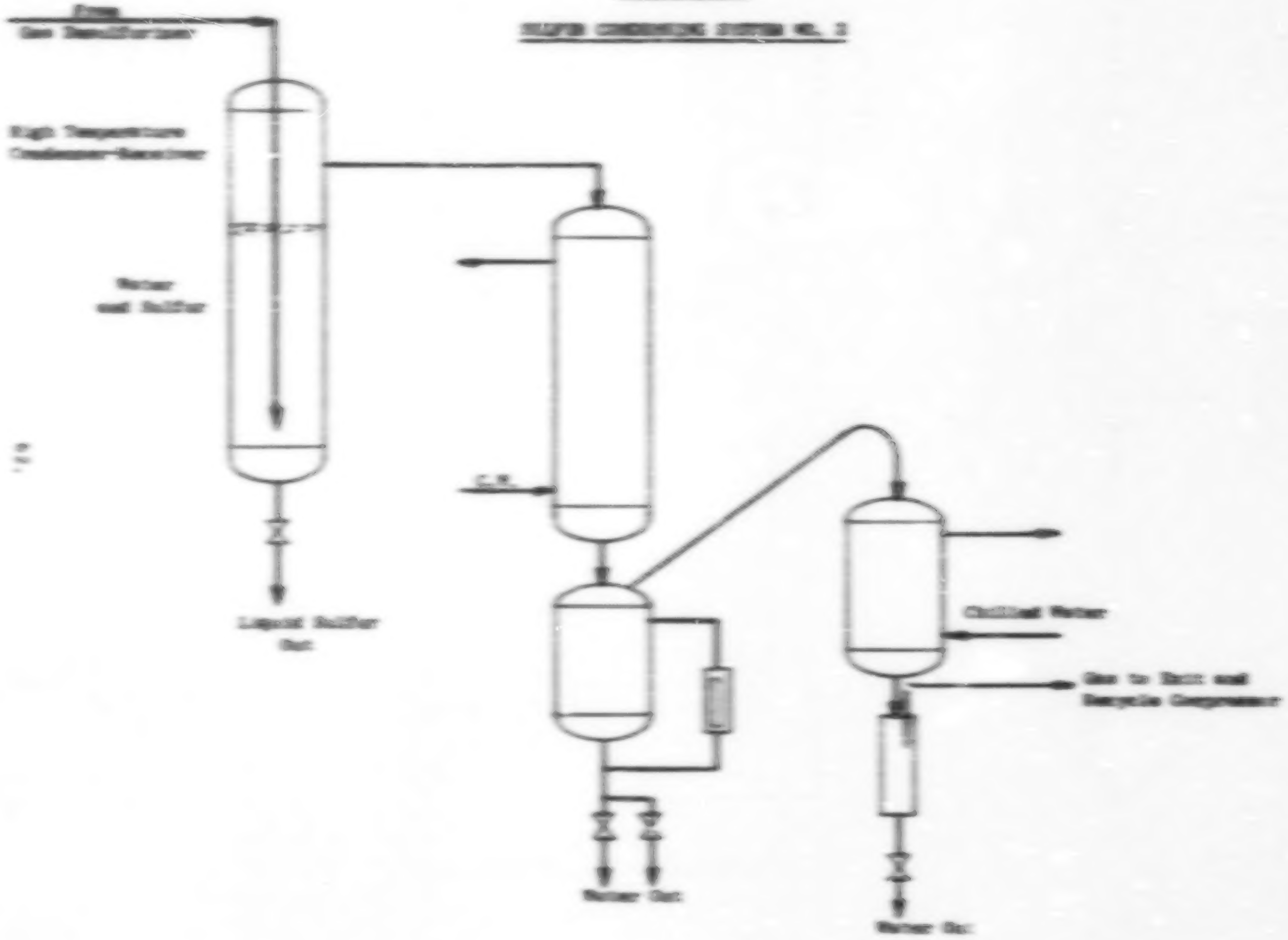

From
Desulfurizer
Steam
High Temperature
Condenser
Steam
Trap
Liquid
Sulfur Out
C.W.
Water and
Sulfur Out
C.W.
Chilled Water
Gas to Unit
and Recycle
Compressor
Water
Out
Water
Out

FIGURE IV-12

SULFUR CONDENSING SYSTEM NO. 2


From
Gas Desulfurizer
High Temperature
Condenser-Receiver
Water
and Sulfur
Liquid Sulfur
Out
C.W.
Water Out
Chilled Water
Gas to Unit and
Recycle Compressor
Water Out

V. MATERIALS: SOURCE, PREPARATION AND ASSAYS

A. Sulfur Acceptors

During operations of the continuous acceptor unit, the following natural stones were used:

1. Tymochtee dolomite, C. E. Duff & Son, Inc., Huntsville, Ohio.
2. Canaan dolomite, Charles Pfizer, Inc., Adams, Mass.
3. Buchanan dolomite, James River Limestone Co., Buchanan, Va.
4. Nebraska limestone, Hopper Brothers Quarries, Weeping Water, Nebraska.
5. Rapid City limestone, Hills Materials Co., Rapid City, S. D.

Assay results for the stones, as used in the experimental program, are given in Table V-1.

The acceptors were ground using a mill which was adjusted to maximize the yield of the desired size fraction. The oversize fraction was reground and the undersize material was set aside. Usually, the material was then wet screened to remove all of the fines. This was necessary to make attrition data obtained in the continuous unit more meaningful. The wet screened acceptor was then dried under infrared lamps. Canaan dolomite was not wet screened since it produced little dust when it was ground.

Table V-2 presents results of elemental analyses on calcined acceptors which were ignited in air. Duplicate analyses on Tymochtee 9, 10 and 11 dolomites are presented. It was thought that the difference in activity observed between the hardened Tymochtee stones might be explained by some element of composition. Reference to Table V-2 shows no obvious reason why this should be so. The Tymochtee stone has impurities consisting mostly of silica and alumina which is to be expected from clay minerals. It is concluded that the difference in activity is not readily explained by the elemental composition of the stone.

The formation of inert "CaO" does seem to parallel the presence of silica impurity in the stone. Tymochtee dolomite had more of this impurity than either Canaan or Buchanan stone and also displayed higher concentrations of "CaO".

B. Acceptor Assays

The assay of fresh acceptors was discussed in detail earlier.(1) A change was made in the assay procedure for sulfided stone. Previously, the $CaCO_3$ content was determined gravimetrically and the CaS content was determined by difference. In the current reporting period, the procedure was changed to allow for the direct determination of the CaS content of the stone. It was found that the total of the CaS and $CaCO_3$ concentrations did not equal 100%. A term was therefore introduced to account for the missing calcium values, and the calcium was assumed to be in the form of CaO since it had earlier been determined that under the conditions of the lab assay, $CaCO_3$ can react with silica in the stone to produce compounds such as $CaO\ (SiO_2)_x$. Under run conditions of the sulfur acceptor cycle, additional $CaCO_3$ is lost via reaction with impurities. This is over and above what reacts in the laboratory assay of the fresh stone.

[illegible]

[illegible]

Stone	[illegible]			[illegible]		[illegible]		[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Calculation Factors									
R_1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
R_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
$R_3^{(1)}$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Mole Ratio Ca/100 grams raw Stone	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Equations:

Let
R_1 = [illegible]
R_2 = [illegible]
R_3 = [illegible]
[illegible] = [illegible]
[illegible] = [illegible]

Then.
R_1 = [illegible]
R_2 = [illegible]
R_3 = [illegible]
R_3 = [illegible]

[illegible]

[illegible] = [illegible]
[illegible] = [illegible]

[illegible]

(1) R_3 = [illegible]

The procedure for determination of CaS in sulfided stone is to first weigh the sample into a 1000 ml flask. About 0.5 to 2.0 grams are used depending on the sulfur content of the stone. To this are added 200 ml of water and 50 ml of 0.1 normal iodine solution. The flask is stirred to wet the stone, and then 100 ml of 1:10 diluted HCl is added to displace sulfur from the stone and to dissolve it completely. The flask is stirred for 30 minutes and then titrated with sodium thiosulfate solution. The sulfur content is calculated according to standard procedures as mols of sulfur or CaS/100 grams of sample.

The $CaCO_3$ and $CaSO_4$ contents of the sample are determined on a separate sample via the gravimetric assay method described earlier,(1) and are put in terms of mols/100 grams of stone. The final piece of data required is the weight of impurities plus MgO/mol of calcium and this is available from the original assay of the raw stone. Then for a 100 gram basis,

$$100 = \text{mols } CaCO_3 \times 100.09 + \text{mols } CaS \times 72.14 + \text{mols "CaO"} \times 56.08$$

$$+ \text{mols } CaSO_4 \times 136.14 + \frac{\text{grams inerts}}{\text{mol calcium}} \times (\text{mols } CaS + CaCO_3 + \text{"CaO"} + CaSO_4).$$

In the above expression, the only unknown is the mols of "CaO" so that the unknown is readily calculated. This was done for each assay.

C. Low-Temperature Ash

The low-temperature ash used for alkali fume removal studies was produced from Illinois No. 6 coal (Consolidation Coal Company's Hillsboro Mine).

The procedures for the ash preparation from unwashed coal are shown in Figure V-1.

The typical conditions for low-temperature char ashing at 538°C (1000°F) are shown in Table V-3 below:

TABLE V-3

Ash from Illinois No. 6 Coal
Pressure: 7.8 atm. (100 psig)

Feedstock	14 x 65 mesh carbonized Illinois No. 6 coal
Temperature, °C (°F)	538 (1000)
Input, SCFH	
Air	6.5
N_2	15

The changes in composition which occurred as the coal was processed are shown in Table V-4. Data are given for both elemental analyses of the ash and for the alkali and chlorine content of the unignited material. In addition, a set of analyses performed by the Illinois State Geological Survey are given. Their determinations of sodium and potassium parallel those of Conoco, but the ISGS number for chlorine in the raw coal was considerably higher. This discrepancy did not extend to the analysis of the carbonized coal.

[illegible]

[illegible]
[illegible]
[illegible]

[illegible]	[illegible]		[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
[illegible]										
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	—	[illegible]	—	[illegible]	—	—	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

FIGURE V-1

Preparation of Low-Temperature Ash

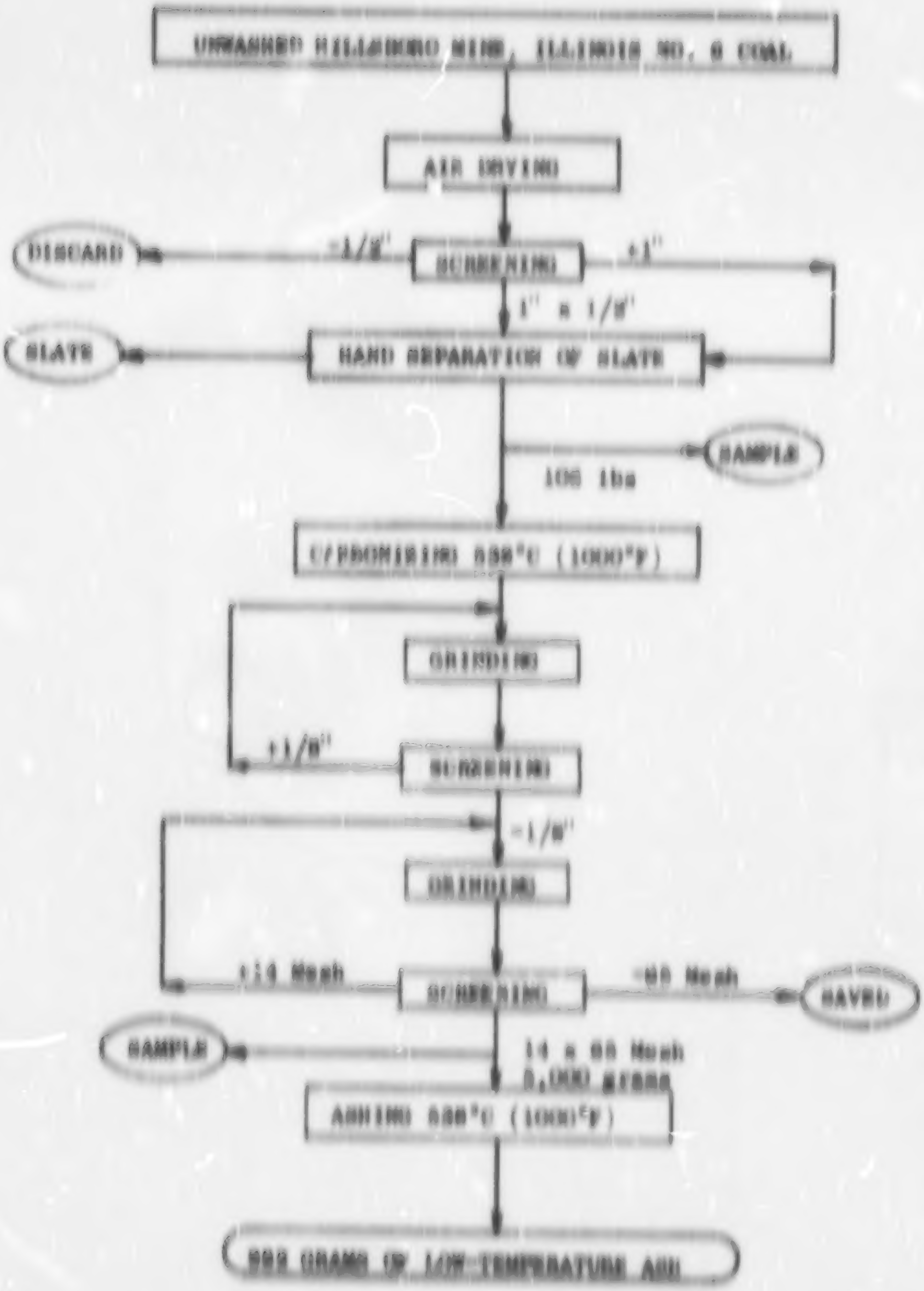

UNWASHED HILLSBORO MINE, ILLINOIS NO. 6 COAL
AIR DRYING
DISCARD
-1/8"
SCREENING
+1"
1" x 1/8"
SLATE
HAND SEPARATION OF SLATE
SAMPLE
106 lbs
CARBONIZING 538°C (1000°F)
GRINDING
+1/8"
SCREENING
-1/8"
GRINDING
+14 Mesh
SCREENING
-65 Mesh
SAVED
SAMPLE
14 x 65 Mesh
5,000 grams
ASHING 538°C (1000°F)
992 GRAMS OF LOW-TEMPERATURE ASH

TABLE V-4

Coal Based Materials for Alkali Vapor Removal Study

	Raw Hillsborough Coal			Carbonized Hillsborough Coal			Low Temperature Ash	
			1965 Assay			1965 Assay	Without Ignition	After Ignition
Whole Sample (dry basis), wt %								
Ash	13.63	—	12.8	13.40	20.63	19.2	—	96.80
Cl	0.26	0.20	0.40	—	0.13	0.11	0.02	0.01
Na	—		0.220			0.227		
K	—		0.187			0.250		
Ash Analysis (a), wt %								
Na_2O	1.50	1.37		1.40	1.47		1.25	1.02
K_2O	1.67	1.72		1.77	1.84		1.63	1.56
CaO	3.86			4.53	3.30		3.35	
MgO	0.70			0.84	0.86		0.82	
Fe_2O_3	21.86			27.47	25.25		20.63	
TiO_2	1.09			0.44	0.51		1.17	
P_2O_5	0.13			0.75	0.38		0.40	
SiO_2	39.23			40.46	44.57		40.72	
Al_2O_3	18.41			19.11	17.58		17.40	
SO_3	3.39			4.23	3.43		3.34	
[illegible]	—			—	—		3.05	
Dry Raw Coal Basis, wt %								
Cl	0.26	0.20	0.40	—	0.086	0.077	0.004	0.001
Na	0.202	0.120	0.220	0.141	0.149	0.160	0.131	0.103
K	0.187	0.250	0.187	0.203	0.203	0.176	0.190	0.176

(a) Ignition carried out in air at 800°C.

The analyses show a moderate loss of sodium from the coal upon low-temperature ashing. It is interesting to note the rather large loss of chlorine which exceeded 90%. It is clear that the low-temperature ash as we made it did not duplicate the input of chlorine which would be obtained from raw coal. To compensate, NaCl was added to the ash as described in Section XI.

Data are given in Table V-8 for the alkali content of Tymochtee and Canaan dolomite fines which were fed to the process. The Tymochtee stone displayed far higher levels of alkali and chlorine than did the Canaan dolomite. The data for Canaan dolomite scatter considerably. This is due to the fact that the analysis used was developed for coal ash, and is set up to detect sodium and potassium in ash on the order of 1% & 0.1%. The weakness of the solids alkali analyses precluded alkali material balances from being made when the balance required knowledge of changes in the alkali content of solids.

TABLE 3-5

Analyses of Dolomite Tests in Alkali Free Removal Study

	Tymochtee 22			Canaan 4				
	Raw	Ignited	Raw	Raw	Raw	Raw	After Lab Aging[b]	Ignited
Whole Sample, Wt. %								
Cl	0.07		0.07		0.01	0.04		
Na			0.19	0.01	0.02	0.04	0.01	
K			0.19	0.02	0.03	0.04	0.02	
Analysis After Ignition,[a] Wt. %								
Na_2O	0.50	0.40						0.02
K_2O	0.40	0.31						0.06
CaO	35.40	38.55						57.37
MgO	34.25	36.51						41.48
Fe_2O_3	0.70	0.56						0.03
TiO_2	0.21	0.08						0.06
P_2O_5	0.01	0.04						0.06
SiO_2	6.61	5.22						0.53
Al_2O_3	1.62	1.38						0.00
SO_3	0.13	0.62						0.43

[a] Ignition carried out in air at 900°C.

[b] Maximum temperature = 760°C (1400°F).

VI. SAMPLE CALCULATIONS

The major thrust of the work performed under this contract was in the performance of sulfidation-regeneration runs. A detailed description of the calculations performed in estimating the number of cycles and the specific run conditions and results was given earlier.(1) The assay calculation procedure was changed, and this was described in Section V. Calculations involved in evaluating the results of the lab-scale Chance runs and alkali fume removal runs were straightforward material balances. Only the estimation of the design make-up rate and specification of the conversion of the sulfur sorbent, and the calculation of normalized density are given here.

A. Calculation of Required Make-Up Rate

First, the run data on regeneration activity as a function of cycles were reviewed. The data were accumulated over an extended period, and in order to maintain consistency, all the runs were worked up keying on the $CaCO_3$ content of the stone. It was felt this would be more reliable than the data derived from gas analyses as the H_2S analyzer had undergone occasional calibration difficulties. In addition, the early runs were made before the H_2S analyzer was delivered.

To obtain a mathematical expression for regeneration activity versus cycles, a least squares analysis was run. The log-log relationship between activity and cycles which results was used in the cycling calculations.

A computer program was written to carry out the cycling calculations. The program is shown in Table VI-1. The starting point of the calculations is an inventory of 100 mols of $CaCO_3$ with no CaS. The inventory is first fed into the gas desulfurizer where it is sulfided at a predetermined level. The degree of sulfidation is set at a constant number of mols or percentage of total calcium. The relative percentage conversion of $CaCO_3$ to CaS therefore increases as the $CaCO_3$ is depleted during cycling. It was assumed that all the $CaCO_3$ in the gas desulfurizer is equally reactive regardless of age. Thus, if 10% is the predetermined conversion of total calcium and 25 mols of $CaCO_3$ enter the gas desulfurizer, the fraction 10/25 of the $CaCO_3$ in each particle is reacted independent of its age and percent $CaCO_3$ content. For example, fresh stone would exit at 40% CaS and a stone entering at 80% would exit at 88.0% CaS.

The inventory then goes into the regenerator where each particle is regenerated according to its age following the fitted relationship which had been worked out based on experimental data. It is assumed that this relation holds regardless of the specific CaS content. As an example, a stone particle one cycle old might have 40% of its CaS content regenerated to $CaCO_3$ while an older stone might have only 5% of its CaS regenerated. The regenerated inventory is then reduced by the amount of the make-up rate, e.g., 5%, and refilled with fresh stone. As the cycle by cycle calculations are continued, the $CaCO_3$ of the inventory falls until an equilibrium level is reached.

TABLE VI-1

Computer Program for Cycling Acceptor

```
CYCLES  20-DEC-76       08:53:51

5       C = 13
10      DIM H(300), J(300), F(300)
20      H(1) = 100
30      J(1) = 0
40      N = 1
70      FOR I = 1 TO 300
80      F(I) = .01*EXP(3.77514 - .431135*LOG(I) )
90      NEXT I
110     T = 0
115     FOR I = 1 TO N
120     T =T + (1 - J(I) ) * H(I)
130     NEXT I
140     FOR I = 1 TO N
150     J(I) = J(I) + C   /T*(1 - J(I) )
160     NEXT I
170     REM  SULFIDATION COMPLETED
180     REM  START REGENERATION
210     FOR I = 1 TO N
250     J(I) = (1-F(N+1-I)) * J(I)
260     H(I) = .98 * H(I)
270     NEXT I
280     REM  END REG'N AND PURGE START MAKEUP
310     N = N + 1
320     H(N) = 2
330     J(N) = 0
390     IF INT( (N-1)/200)*200 = N-1 THEN 410
400     GO TO 110
410     PAUSE
411     PRINT "INPUT STEP NUMBER";
412     INPUT Q
415     PRINT "AGE, CYCLES"; TAB(15); "MOLS"; TAB(25); "% CAS"; TAB(35);
 "MOLS CACO3"
420     FOR I = 1 TO N STEP Q
430     PRINT DEC(N-I,6,0); DEC(H(I),17,2); DEC(100*J(I),22,1); DEC((1-J
(I))*H(I), 18,3)
440     NEXT I
445     PRINT "T = ";DEC(T,8,2)
450     PRINT
460     PAUSE
470     GO TO 110
480     END
READY
```

Where:

H(I) = Number of mols of calcium aged I cycles.
J(I) = Fraction CaS in particles aged I cycles.
T = Total mols $CaCO_3$ entering the gas desulfurizer.
C = Percent conversion of total calcium to CaS in the gas desulfurizer.
N = Number of cycles processed so far.
F(I) = Fractional regeneration of CaS to $CaCO_3$ in Cycle I.

Table VI-2 is the computer output for Canaan dolomite cycled 200 times at 5% makeup and 15% sulfidation per pass. Although every cycle was calculated, only every fifth cycle was printed out.

Each computer run gives an equilibrium $CaCO_3$ value for a given make-up rate, sulfidation level, and regeneration cycles relation. Runs are made until a line for the equilibrium $CaCO_3$ content versus percent conversion can be drawn. As the sulfidation per cycle increases, the equilibrium $CaCO_3$ content decreases.

Using the data generated experimentally for regeneration activity versus cycles, the equilibrium $CaCO_3$ content for Canaan dolomite, Tymochtee dolomite and Buchanan dolomite hardened at 30% conversion were calculated. The results are shown in Figures VI-1 to VI-3, respectively. However, another calculation was necessary in order to set the design for the system.

It was determined that, in order to prevent breakthrough of H_2S, some excess $CaCO_3$ must be present in the gas desulfurizer reactor. The design constraint was that the ratio of mols H_2S per hour fed:$CaCO_3$ in the bed should not exceed 3.6. An additional constraint was that the solids residence time in the gas desulfurizer was to be 20 minutes. Then the following calculation was made:

Let Q = the molar feed rate of total Ca/hr,

then the number of mols of total Ca in the bed are Q/3.

Let V = the mols/hr of $CaCO_3$ leaving the bed,

then the fraction of $CaCO_3$ leaving the bed = the fraction of $CaCO_3$ in the bed = V/Q.

and the mols of $CaCO_3$ in the bed = V/Q x Q/3 = V/3.

Let X = mols/hr of H_2S fed ≅ mols/hr H_2S reacted = mols/hr $CaCO_3$ reacted.

Using the design constraint for the H_2S-to-$CaCO_3$ ratio gives,

$$3.6 = \frac{X}{V/3} = \frac{3X}{V} \quad \text{or} \quad V = \frac{X}{1.2}$$

Now, $CaCO_3$ fed = $CaCO_3$ reacted + $CaCO_3$ leaving,

$$\text{or } CaCO_3 \text{ fed} = X + V = X + \frac{X}{1.2} = 1.83\,X$$

Stated in words, the $CaCO_3$ fed must be 1.83 times the $CaCO_3$ converted.

This is expressed graphically in Figures VI-1 to VI-3 as a line having a slope of 1.83. The intersection of this line with the line defining the equilibrium $CaCO_3$ content is a point which satisfies both the make-up rate requirement and the requirement for excess $CaCO_3$ in the bed. Results of these calculations are discussed in Section XVI.

TABLE VI-2

Computer Output for Canaan Dolomite
5% Makeup Rate,
15% Sulfidation,
200 Cycles

```
AGE, CYCLES    MOLS        % CAS     MOLS CACO3
   200.        1.76 (1)    94.7       0.093
   195.        0.04        94.7       0.002
   190.        0.04        94.6       0.002
   185.        0.05        94.6       0.003
   180.        0.05        94.5       0.003
   175.        0.06        94.4       0.003
   170.        0.06        94.4       0.004
   165.        0.07        94.3       0.004
   160.        0.08        94.2       0.005
   155.        0.09        94.1       0.005
   150.        0.10        94.1       0.006
   145.        0.11        94.0       0.006
   140.        0.12        93.9       0.007
   135.        0.13        93.8       0.008
   130.        0.14        93.7       0.009
   125.        0.16        93.6       0.010
   120.        0.18        93.5       0.010
   115.        0.20        93.3       0.013
   110.        0.22        93.2       0.015
   105.        0.24        93.1       0.017
   100.        0.27        92.9       0.019
    95.        0.30        92.8       0.021
    90.        0.33        92.6       0.024
    85.        0.36        92.4       0.027
    80.        0.40        92.2       0.031
    75.        0.44        92.0       0.035
    70.        0.49        91.8       0.040
    65.        0.54        91.5       0.046
    60.        0.60        91.2       0.052
    55.        0.66        90.9       0.058
    50.        0.73        90.5       0.069
    45.        0.81        90.1       0.080
    40.        0.89        89.5       0.093
    35.        0.99        88.9       0.109
    30.        1.09        88.2       0.129
    25.        1.21        87.3       0.156
    20.        1.34        86.2       0.187
    15.        1.48        84.7       0.226
    10.        1.63        82.6       0.288
     5.        1.81        78.7       0.385
     0.        0.00         0.0       0.000
 Y =  15.58  Mols CaCO3 Total
```

(1) This figure is the residual of the starting inventory. It represents 0.6% of the total $CaCO_3$, and running the program out to more cycles would not change the total $CaCO_3$ content of the equilibrated inventory.

FIGURE VI-1

Equilibrium $CaCO_3$ in Canaan Dolomite As A Function Of Conversion And Makeup Rate

Temperature = 704°C (1300°F)

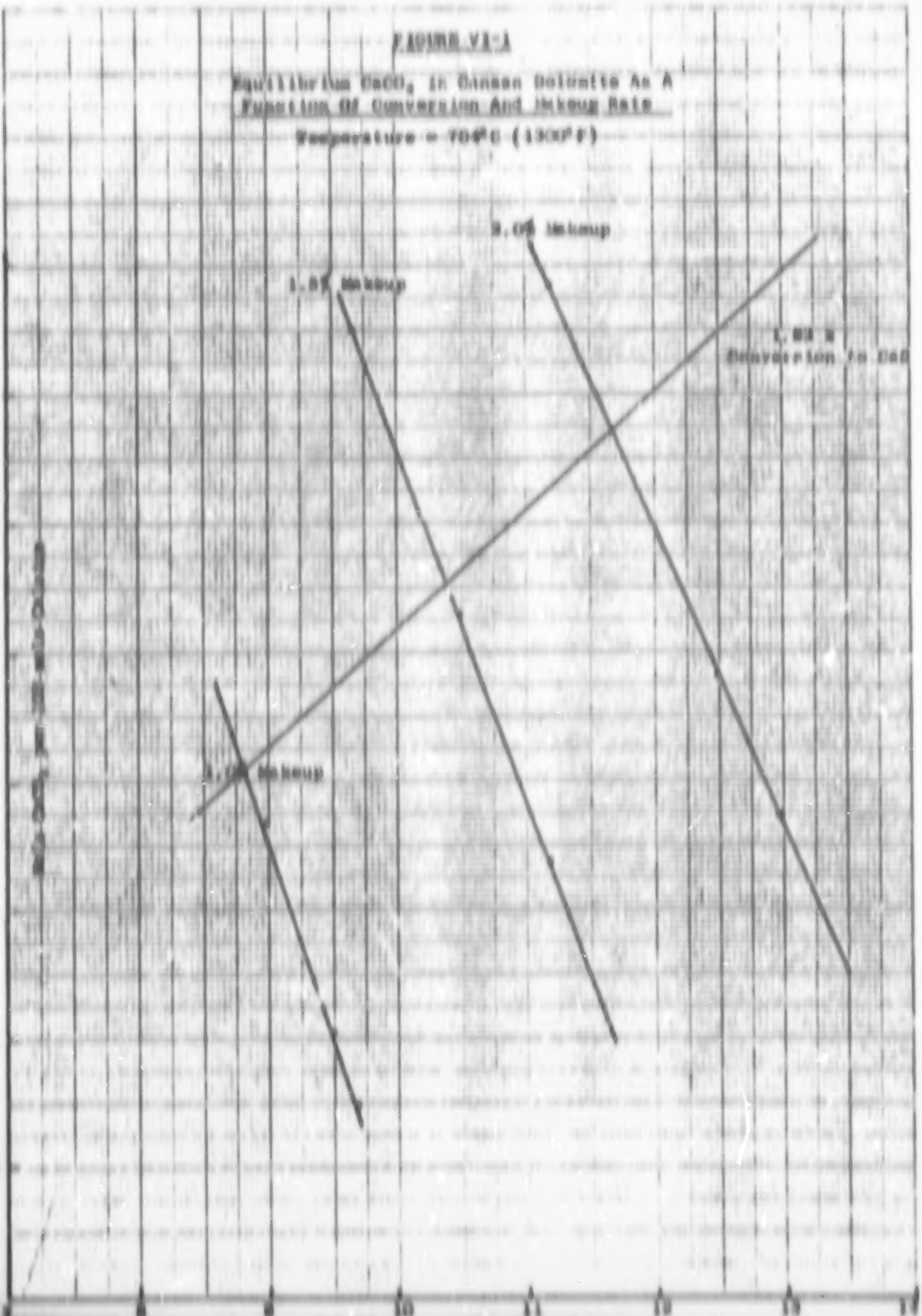
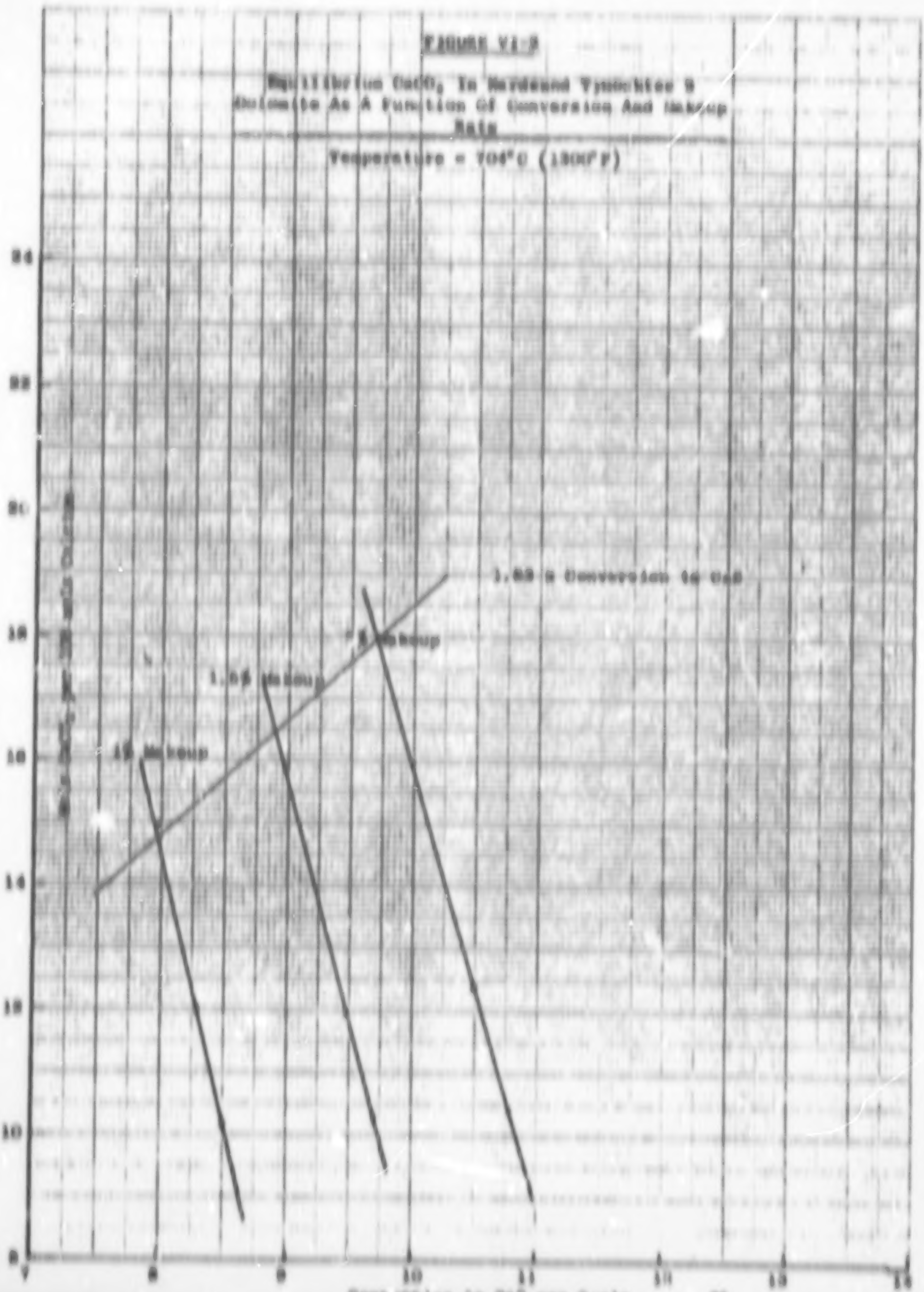


FIGURE VI-9

Equilibrium $CaCO_3$ In Hardened Tymochtee B Dolomite As A Function Of Conversion And Makeup Rate

Temperature = 704°C (1300°F)



76.

B. Calculation of Normalized Density

The normalized density is calculated from the observed density and composition of a stone sample. As the observed density is a function of the molecular weight of the components as well as the structure of the stone, it is desirable to normalize the density to a common basis. The basis chosen was to treat all components as if they were CaO. The procedure is outlined below. Using a basis of one mol, the molecular weight of the stone is calculated using its known composition and content of impurities, MgO plus inerts. This is compared with the weight of the same stone if it were to consist only of CaO and impurities. The ratio of the CaO weight to the actual weight times the observed density is the normalized density.

Basis: 1 gram mol of stone

Component	Run A22 Oxidized Feed Mols	 Grams	Normalized Stone Mols	 Grams
$CaCO_3$	0.698	69.86	0.0	--
CaS	0.031	2.24	0.0	--
$CaSO_4$	0.193	26.28	0.0	--
"CaO"	0.078	4.37	1.00	56.08
MgO + Inerts	--	44.00	--	44.00
		146.75		100.08

Density = 1.99 gm/cc

Normalized Density = $\frac{100.08}{146.75}$ x 1.99 = 1.36 gm/cc.

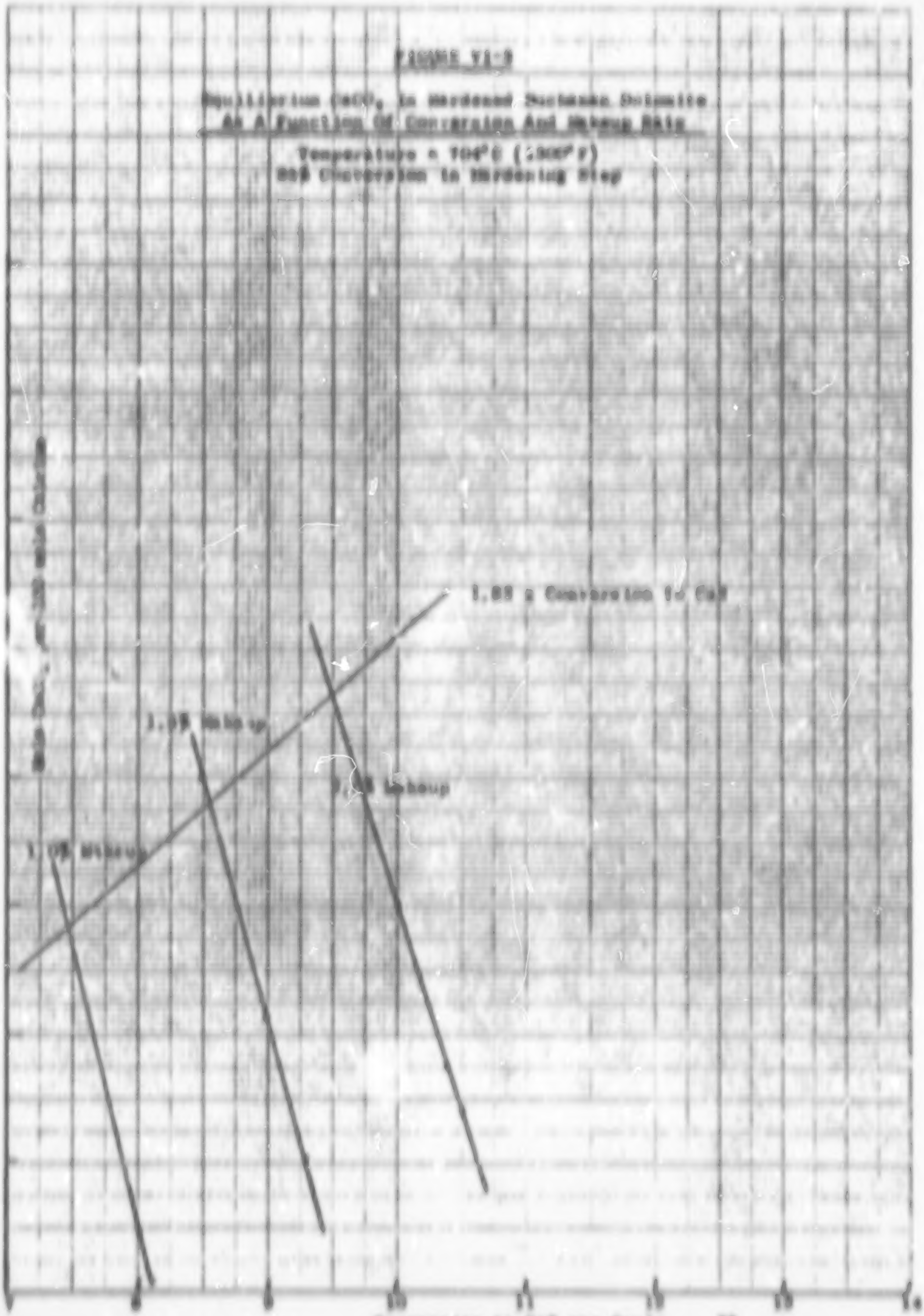


FIGURE VI-9

Equilibrium CaCO$_3$ in Hardened Dolomite As A Function Of Conversion And Makeup Rate

Temperature = 704°C (1300°F)

80% Conversion in Hardening Step

VII. TABULAR CHRONOLOGICAL HISTORY OF RUNS

The purpose, general run conditions, and conclusions drawn for all runs made in the course of this contract period are given in the tables listed below. All the runs were made at a pressure of 15 atmospheres.

TABLE	
VII-1	Summary of Initial Runs with Canaan Dolomite
VII-2	Summary of Early Hardening Runs
VII-3	Summary of Runs with Sorbent at Various Hardening Conditions
VII-4	Summary of Chance Product Runs
VII-5	Summary of Main Body of Continuous Runs
VII-6	Batch Studies of Process Variables
VII-7	Summary of $CaSO_4$ Reduction by H_2S
VII-8	Low-Temperature Ashing of Coal
VII-9	Alkali Fume Removal

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE [illegible] (Cont'd.)

Summary of Runs with [illegible] from Various Hardening Conditions

Run Number	[illegible]	[illegible]	[illegible]	[illegible]
Unit Configuration	Sulfidation-Regeneration (continuous cycling setup, preceded by hardening step)	Sulfidation-Regeneration (continuous cycling setup preceded by hardening step)	Sulfidation-Regeneration (continuous cycling setup preceded by hardening step without use of sulfur)	Sulfidation-Regeneration (continuous cycling setup)
Date of Run	[illegible], 1974	[illegible], 1974	[illegible], 1974	[illegible], 1975
Run Duration with [illegible], hrs.	[illegible]	[illegible]	[illegible]	[illegible]
Purpose of Run	To determine attrition resistance of hardened stone [illegible]	To determine attrition rate of stone hardened at mild conditions	To determine whether sulfur involvement in the hardening step is necessary	To check the attrition rate of untreated Tymochtee dolomite
Temperature, °C (°F)	[illegible]	[illegible] Sulfidation, [illegible] Regeneration	[illegible] Sulfidation, [illegible] Regeneration	[illegible] Sulfidation, [illegible] Regeneration
Bed Material	Half-Calcined, sulfided Tymochtee dolomite [illegible]	Half-Calcined, sulfided Tymochtee dolomite, [illegible]	Half-Calcined, sulfided Tymochtee dolomite, [illegible]	Half-Calcined, sulfided Tymochtee dolomite [illegible]
Feedstock	[illegible] mesh Tymochtee dolomite, shipment No. [illegible]	[illegible] mesh Tymochtee dolomite, shipment No. [illegible]	[illegible] mesh Tymochtee dolomite, shipment No. [illegible]	[illegible] mesh Tymochtee dolomite, shipment No.
Shutdown	Voluntarily	Voluntarily	[illegible]	[illegible]
Results and Conclusions	[illegible]	[illegible]	[illegible]	[illegible]

TABLE VII-4

Summary of Clinker Product Runs

Run Number	L-1	L-2	A-62
Unit Configuration	Setup for clinker product feed experiment	Setup for clinker product feed experiment	Feed system and collecting system for use of $CaCO_3$ slurry
Date of Run	6/12-6/14, 1974	6/18, 1974	2/10-2/12, 1975
Run Duration with H_2S Feed, hrs.	6.5	3.5	H_2S and $Ca(NO_3)_2$ solution fed for 40 minutes
Purpose of Run	To determine, whether fine limestone can act as sulfur acceptor in calcined form	To determine, whether fine limestone can act as sulfur acceptor in calcined form	Establish feasibility of using $Ca(NO_3)_2$ solution in water to disperse most of calcium salt into hot bed of Magnesite for formation of fine CaO which would act as a sulfur acceptor
Temperature, °C (°F)	927 (1700) calcination and sulfidation	927 (1700) calcination and sulfidation	927 (1700)
Bed Material	20 x 35 mesh dead burned dolomite	35 x 48 mesh Magnesite (electrofused, ground MgO)	48 x 65 mesh Magnesite
Feedstock	65 x 150 mesh Nebraska Limestone	150 x 200 mesh Nebraska Limestone	Saturated solution at 70°F in water
Shutdown	Voluntarily	Voluntarily	Involuntarily, slugging and plugging in the hot section of feed line
Results and Conclusions	Sulfidation does not proceed to completion, decrease limestone size, dead burned dolomite is active toward H_2S	Sulfidation did not proceed to completion	$Ca(NO_3)_2$ melts as water evaporates, and then agglomerates

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

Run Number	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Unit Configuration	Regeneration	Sulfation/Regeneration	Sulfation/Regeneration	Sulfation	Sulfation
Date of Run	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Purpose of Run(s)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Temperature, °C (°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Bed Material	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Shutdown	Voluntarily	Voluntarily	Voluntarily	Voluntarily	[illegible]
Results and Conclusions	[illegible]	[illegible]	[illegible]	[illegible]	To be determined

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	Volumetrically	Volumetrically	Volumetrically	Volumetrically	Volumetrically
Results and Conclusions	To be determined	[illegible]	To be determined	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

Run Number	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Unit Configuration	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Date of Run	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Run Duration with SO₂ Feed, hrs.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Purpose of Run	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Temperature, °C (°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Bed Material	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Problems	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Results and Conclusions	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE VII-8

Low Temperature Ashing of Coal

Run; Low temperature ashing of Hillsboro mine coal (Illinois No. 6 coal).

Unit Configuration; 4" diameter reactor provided with a dip leg extending to the bottom of reactor for introduction of air and diluting inert gas.

Date of Run; 5/14-5/30, 1975

Purpose of Run; To prepare feedstock for alkali fume removal type of runs.

Temperature; ≈ 538°C (1000°F)

Bed Material; Batch of char prepared by low temperature carbonization of Illinois No. 6 coal.

Shutdowns;

1. Higher than anticipated pressure drop through apparatus; increased working pressure from 3 atm to 7 atm.
2. A poor heat dissipation in stationary bed; increased total gas throughput for bed fluidization.

Results and Conclusions; Good heat dissipation in fluidized bed of char, increased air flowrate possible.

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

VIII. CYCLIC CONTINUOUS RUNS WITH CANAAN DOLOMITE

A. Introduction

The reaction,

$$CaCO_3 + H_2S = CaS + H_2O + CO_2$$

is used for both gas desulfurization and sorbent regeneration. Conditions in the gas desulfurizer and regenerator are such that the equilibrium H_2S content of the desulfurized fuel gas is low, and the equilibrium H_2S content of the regenerator offgas is relatively high.

Run conditions in this study generally simulated those in process vessels as given below:

	Gas Desulfurizer	Regenerator
Temperature, °C (°F)	871 (1600)	760 (1400)
Inlet Gas Composition, Mol %		
H_2	16	--
CO	19	--
CO_2	8	66
N_2	46	--
H_2S	ca. 1	--
H_2O	10	34
Mol % of Sorbent Ca Reacted/cycle	10-15	--

Canaan dolomite served as the criterion to which all other stones were compared with respect to the critical characteristics of reactivity toward H_2S, regeneration activity, and attrition resistance. To improve operability, a little hydrogen was added to the regenerator to inhibit dissociation of H_2S.

B. Runs Without Makeup

Reactor conditions and results for the gas desulfurizer and regenerator are given in Tables VIII-1 and VIII-2, respectively. Detailed tables for stone composition, H_2S content of exit gas, and attrition as a function of cycles are presented in Appendix B. The data for solids composition include a term for "CaO". This is to account for about 8% of the calcium which is assumed to react with impurities in the stone thereby becoming unavailable for reaction with H_2S.

The "CaO" is determined by deducting the assayed values of CaS and $CaCO_3$ from 100%. In all Canaan dolomite runs, the attrition rate was about 1% of the circulation rate and the H_2S concentration in the desulfurizer offgas was less than 0.03 mol % prior to breakthrough.

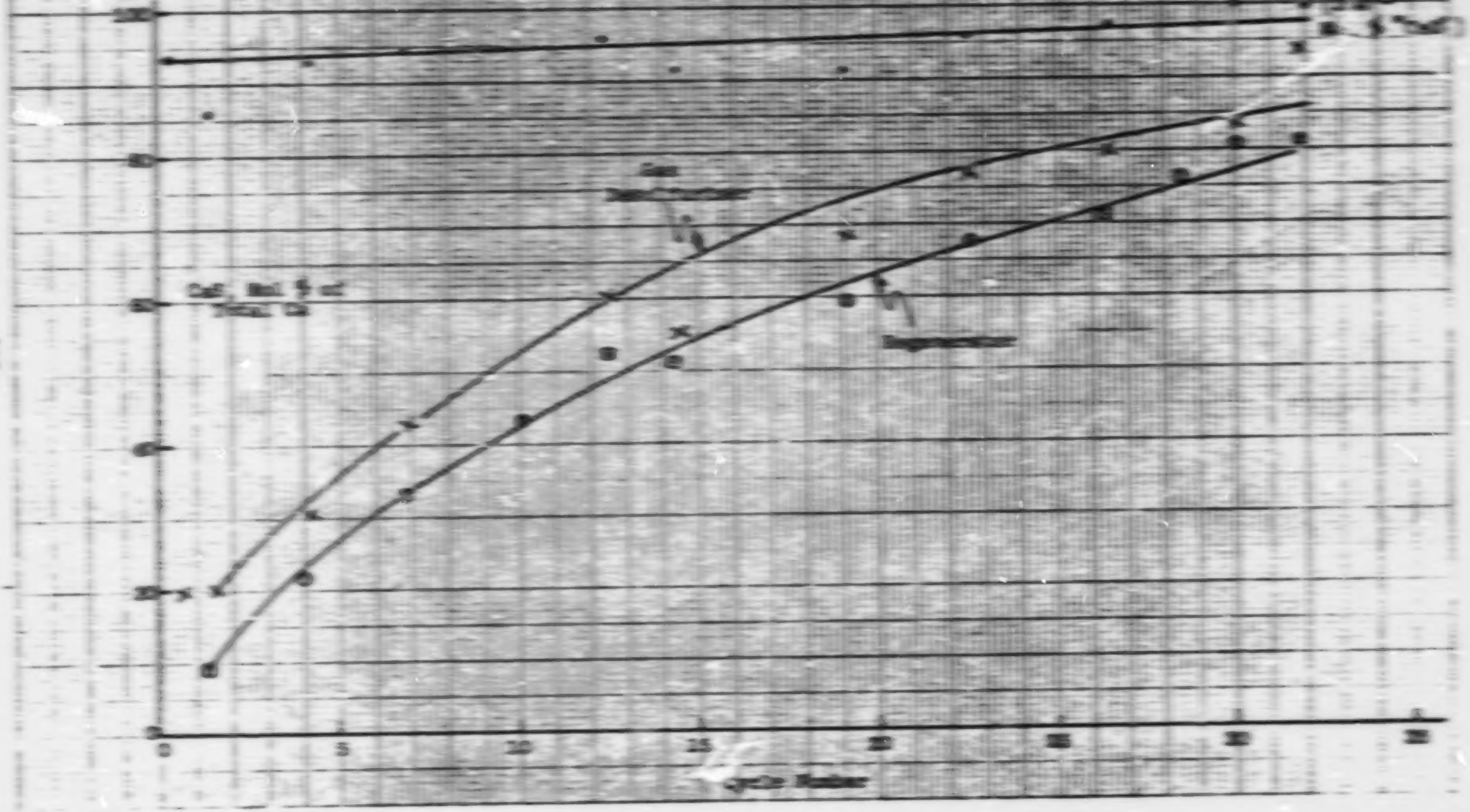
Run A80A

Run A80A was similar to Run A7 of 1979, except that the molar conversion to CaS was 13% per pass instead of 30%. The progress of the run as defined by the CaS content of solids leaving the gas desulfurizer and regenerator is shown graphically in Figure VIII-1 as a function of the number of cycles. A total of 33 cycles was achieved before depletion of the inventory due to attrition and sampling forced shutdown.

[illegible]

[illegible]

[illegible]



100
80
60
40
20
0
0
5
10
15
20
25
30
35
Cycle Number

The stone remained reactive toward H_2S throughout the run; there was no breakthrough of H_2S in the gas desulfurizer even at the end when only 10 mol % of $CaCO_3$ was left in the stone. The attrition rate for the entire run was 0.7% of the stone fed.

Regeneration activity was correlated using percent regeneration, or mols of CaS converted to $CaCO_3$/100 mols of CaS fed to the regenerator. The data were plotted on log-log coordinates using number of cycles as the abscissa.

The percent regeneration can be determined in two ways. The first is to take the difference between the CaS or $CaCO_3$ content curves and divide by the CaS content leaving the gas desulfurizer. Due to the residence time in the regenerator, the point equivalent to n cycles on the gas desulfurizer curve is displaced to about n + .3 cycles on the regenerator curve. The method is most accurate when the curves have zero slope. The other method is to determine the moles of H_2S in the regenerator offgas, put this in terms of the change in CaS concentration and divide by the CaS content leaving the gas desulfurizer. The two methods are generally in close agreement. All the regeneration data in this chapter were determined by difference between smoothed solid concentration curves.

Figure VIII-2 shows the results of these calculations for Run A20A and several others.

The data correlated in Figure VIII-2 fit a straight line. The decline in activity in going from 50 to 100 cycles is proportionately the same as going from 5 to 7 cycles when a linear log-log relationship is obtained. The stone should therefore continue to be active long enough to achieve a low make-up requirement.

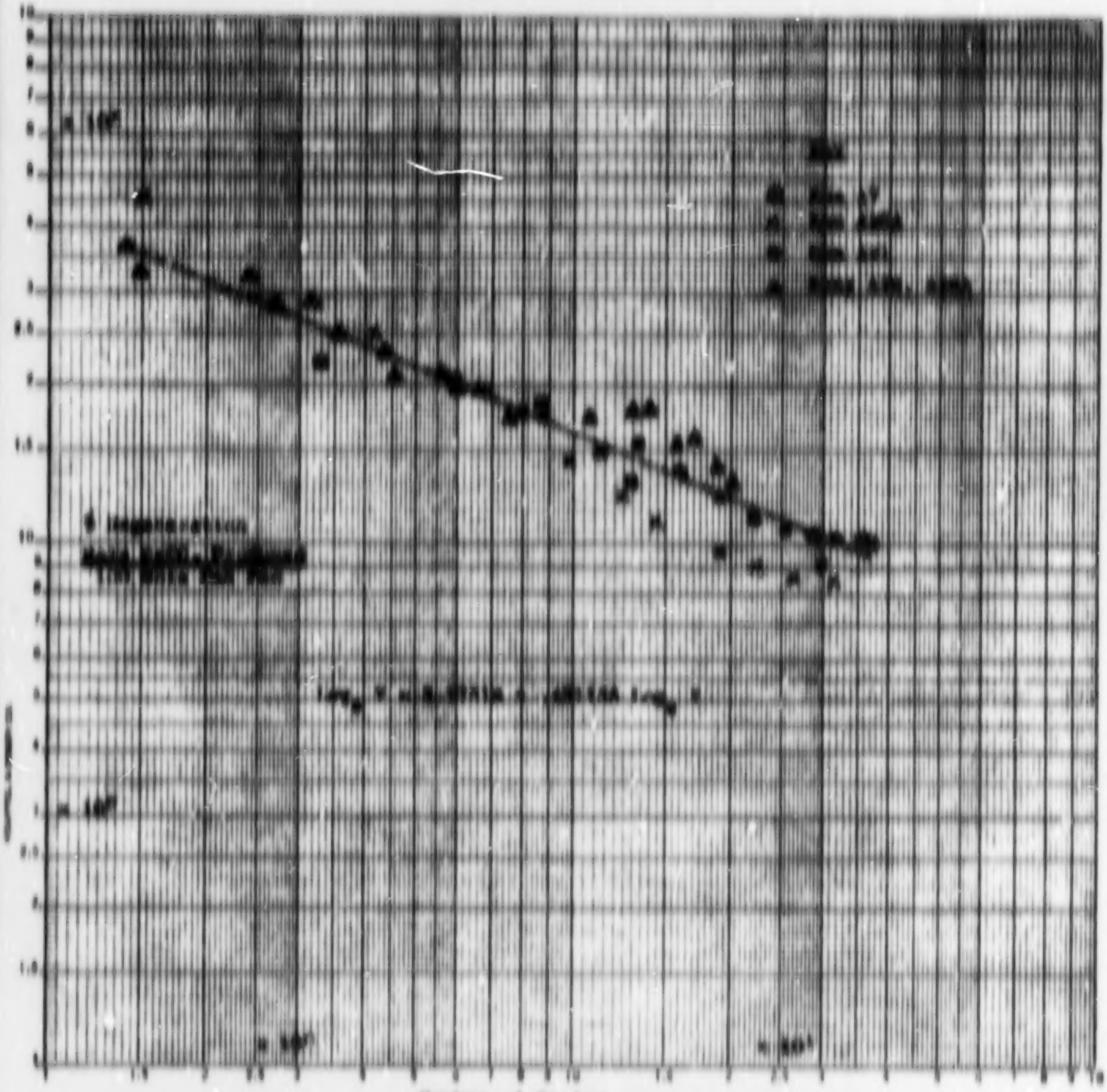
Run A21

Run A21 was made at the same conditions as Run A20A except that recycle gas was used in the regenerator. This allowed the H_2S concentration in the exit gas to more closely approach the equilibrium value. Run conditions are given in Tables VIII-1 and 2, and analyses of exit gases and solids are given in Appendix B. The progress of the run as defined by the CaS content of acceptor is given in Figure III-3. The exit H_2S concentration, as determined by the continuous analyzer was 65-75% of equilibrium during the course of the run compared to ca. 30% in Run A20A. The data for Run A21 in Figure VIII-2 were in good agreement with those of Run A20A, and it was concluded that the rate of regeneration was unaffected by the increased H_2S concentration. The run continued for 36.7 cycles making it the longest run with Canaan stone. There was no H_2S breakthrough and no sign of deactivation of $CaCO_3$ with respect to pickup of H_2S. The data indicate that deactivation with respect to regeneration was the same in Runs A21 and A20A.

In examining approach to equilibrium, regenerator data for H_2S concentration were used. Some results are summarized below. Large differences in approach to equilibrium and kinetic driving force are apparent, yet there was no effect on the overall rate of regeneration. This is consistent with the mechanism of inactive CaS being the limiting factor in regeneration.

FIGURE VIII-8

DEACTIVATION OF CaS IN CANAAN DOLOMITE AT 704°C (1300°F)



Run No.	Cycle No.	Percent H_2S Top of Bed	Percent H_2S Bottom of Bed	Percent H_2S Avg.	Top of Bed, Equilibrium, %	Average Equilibrium, %
A31	18	2.50	1.57	2.04	74	47
A28A	20	0.75	0	0.38	22	11

In a run with hardened Tymochtee dolomite (Section IX-B), the measured H_2S concentration in the exit gas was at 90% of equilibrium. In that run, there was also no indication that the regeneration rate was slowed by the high H_2S content of the gas. It is concluded that the regeneration reaction is intrinsically fast for that fraction of the CaS which is reactive, and that the conversion of stone is not slowed by the presence of product gas at the solids residence times employed in this system. There clearly is no difficulty in attaining the equilibrium concentration of H_2S in the exit gas at 704°C (1300°F).

It must be emphasized that the continuous runs without makeup produced a regenerator feed of varying active CaS content which made it impractical to maintain an exit gas concentration close to the equilibrium value. As the stone activity declined, the H_2S content of regenerator offgas varied, and there was no attempt to keep it close to equilibrium.

Run A28A

Run A28A was made with the regenerator at 760°C (1400°F). Regeneration at cycle 10 improved from about 16% at 704°C (1300°F) to 33% at 760°C. Progress of the run in terms of solids concentration is shown in Figure VIII-4. Due to the improved regeneration, the CaS content of the acceptor rose more slowly than in previous runs.

Regeneration activity as a function of cycles is presented in Figure VIII-3. Results are presented together with data for 704°C taken from Figure VIII-2 and data for 593°C taken from Runs A15 and A16.(1) The lines drawn are roughly parallel.

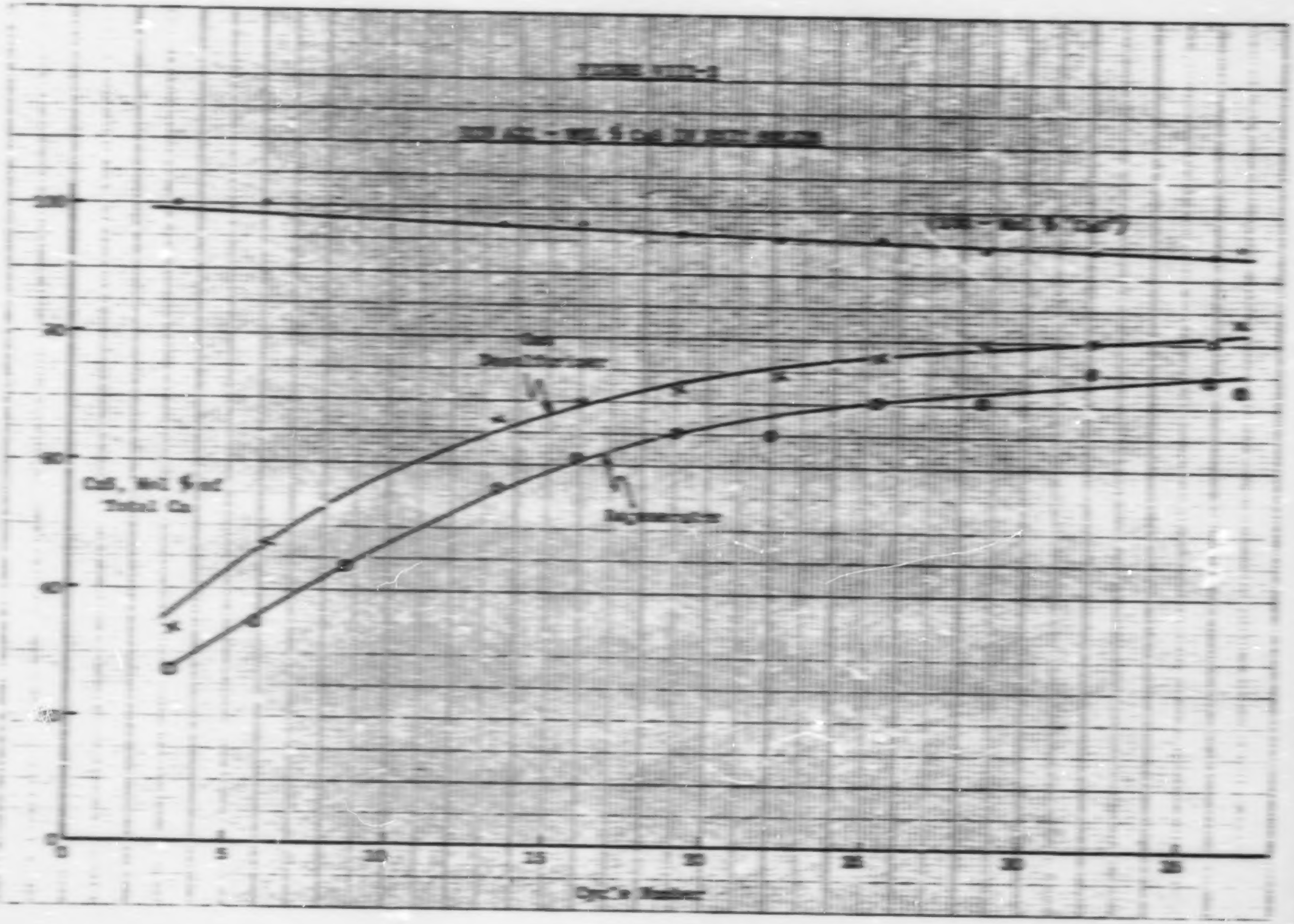
Runs A36 and A36A

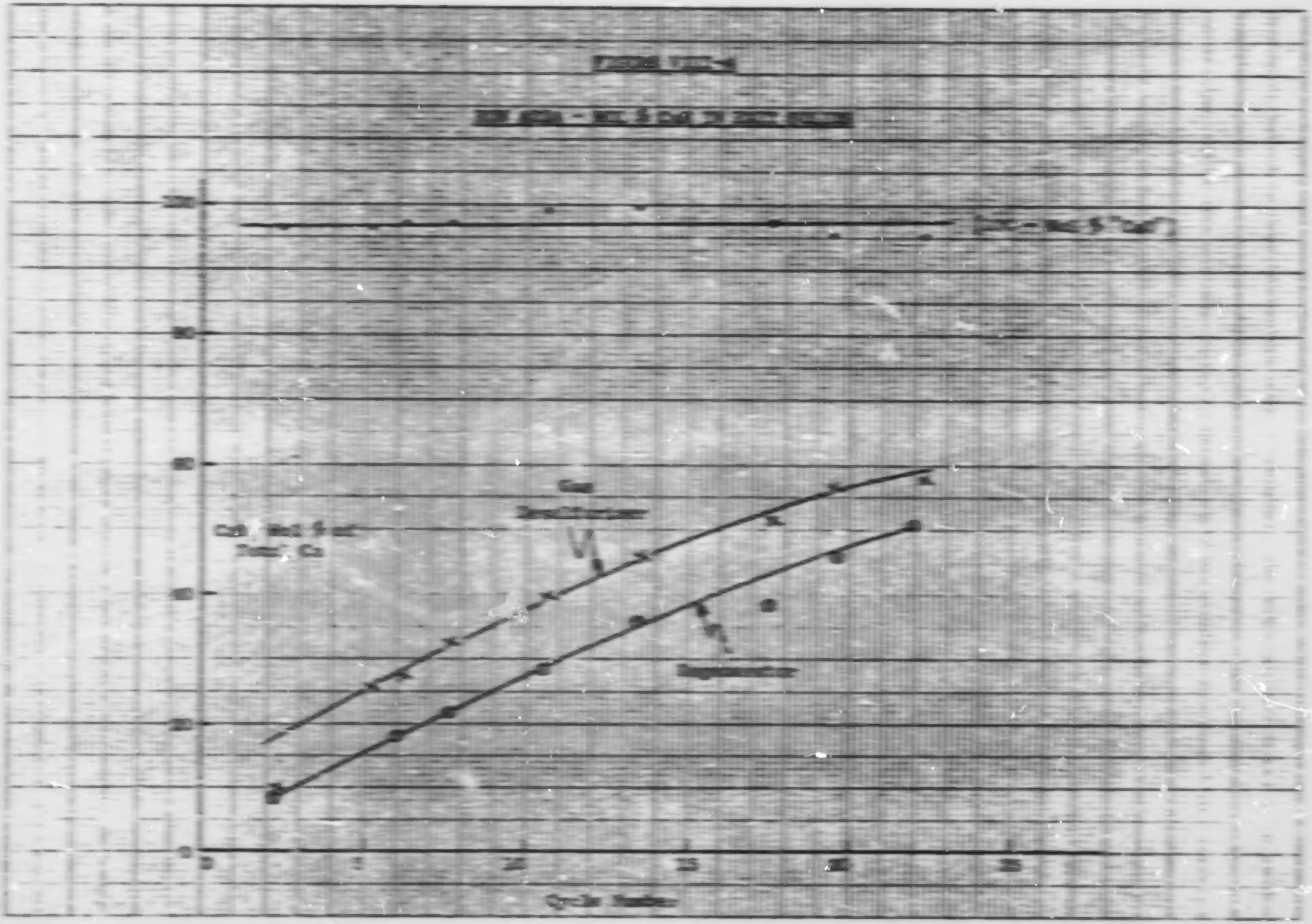
Runs A36 and A36A were duplicate runs. Several operating shutdowns were experienced in Run A36, and it was decided to repeat the run. Stone in the 20 x 28 size consist was fed to determine the effect of particle size. As shown in Table VIII-1, the attrition rate was nominally 1.7%, but this includes ca. 30% +100 mesh material. The larger fluidizing velocity required by the 20 x 28 mesh particles caused solids which would normally be retained in the bed to be blown out. The problem was aggravated by the straight side of the vessel (no disengaging zone) and the restriction above the bed entailed by use of a preheat coil.

Sulfur absorption and regeneration activities were the same as with 35 x 48 mesh stone. The run progress is detailed graphically in Figure VIII-6.

Run A45

Results for this run are presented graphically in Figures VIII-7 and VIII-8.


(100 - Mol % CuO)
Gas
Desulfurizer
Regenerator
CuS, Mol % of
Total Cu
0
20
40
60
80
100
0
5
10
15
20
25
30
35
Cycle Number



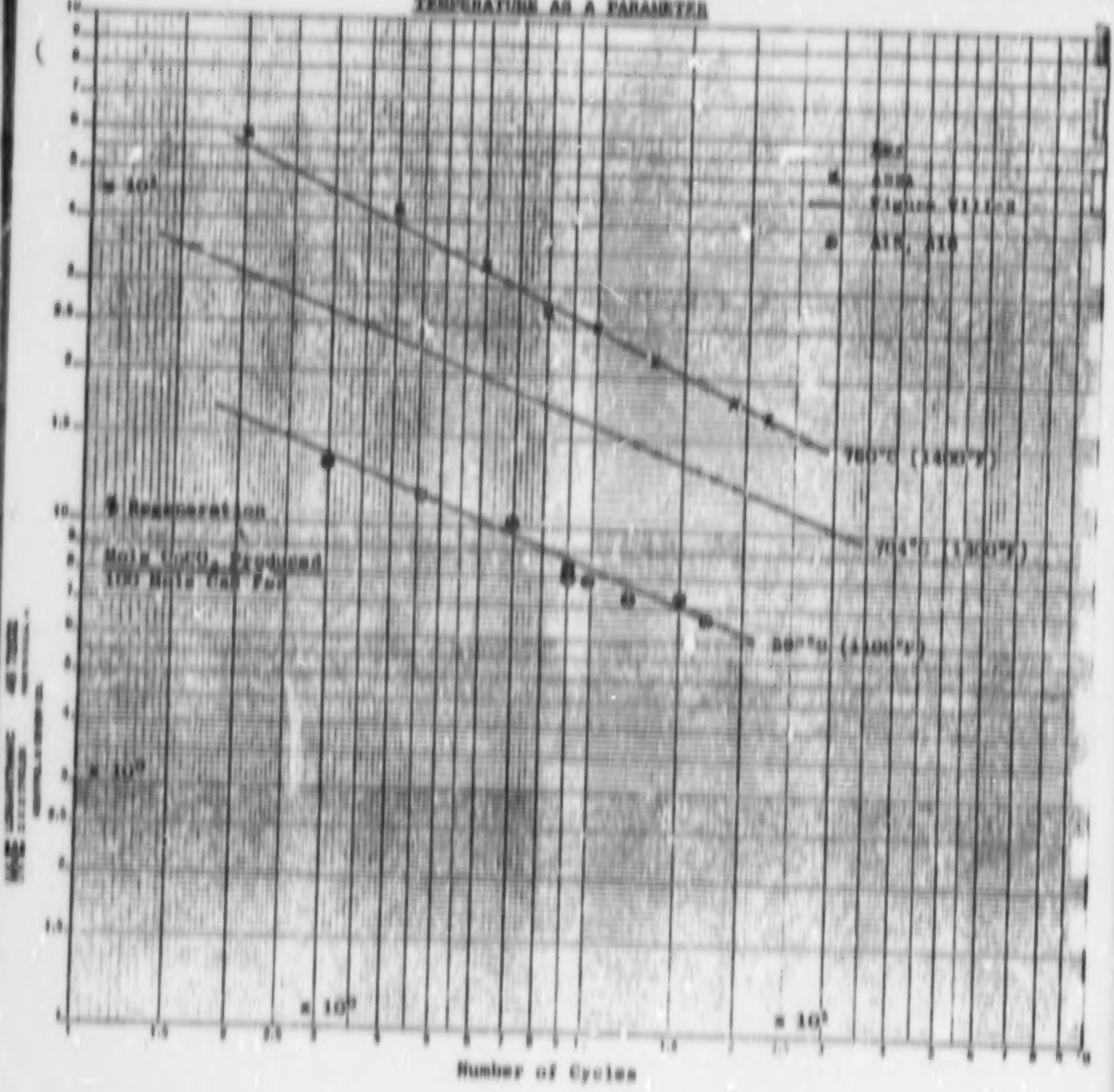
[illegible]

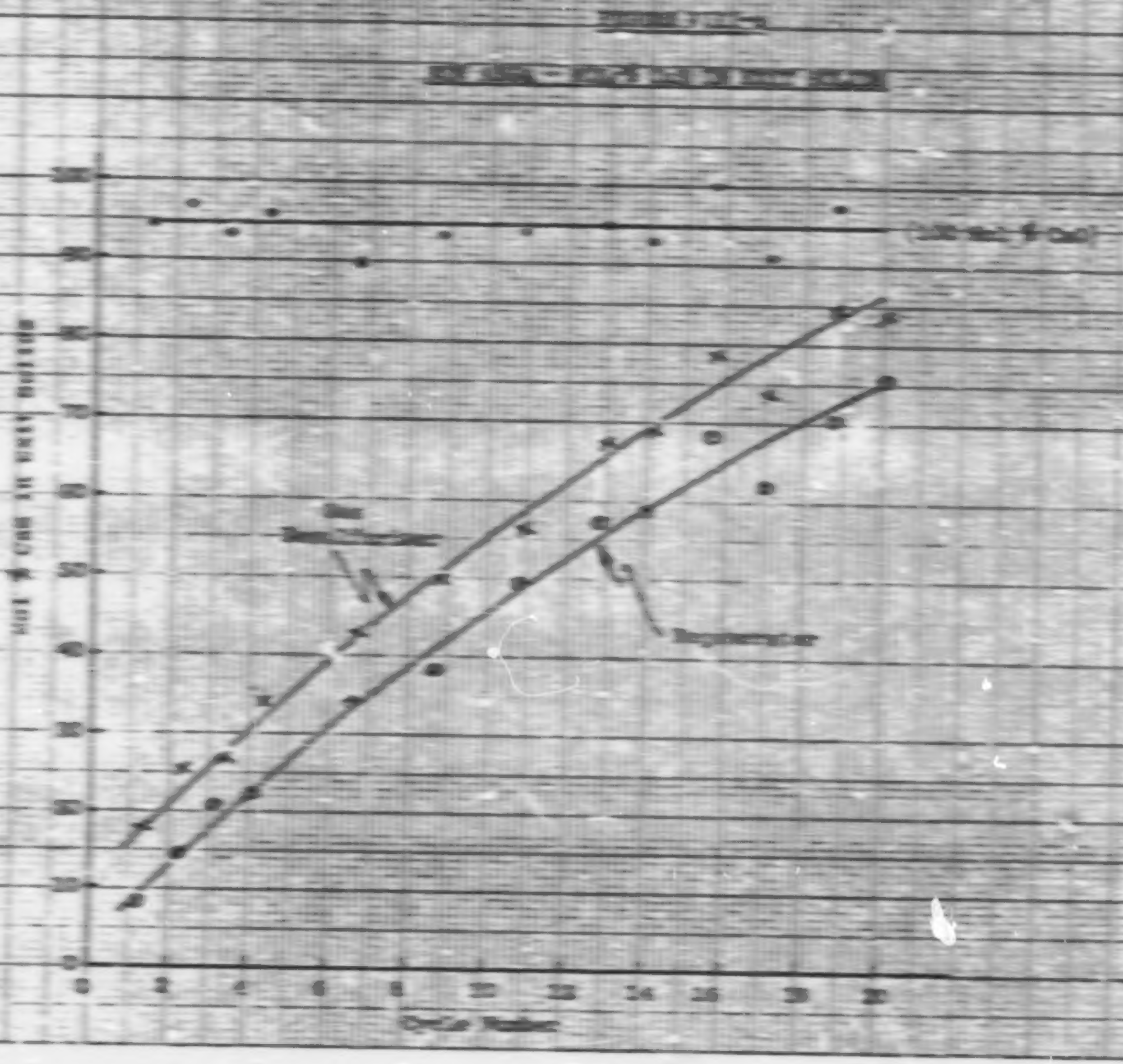
[illegible]

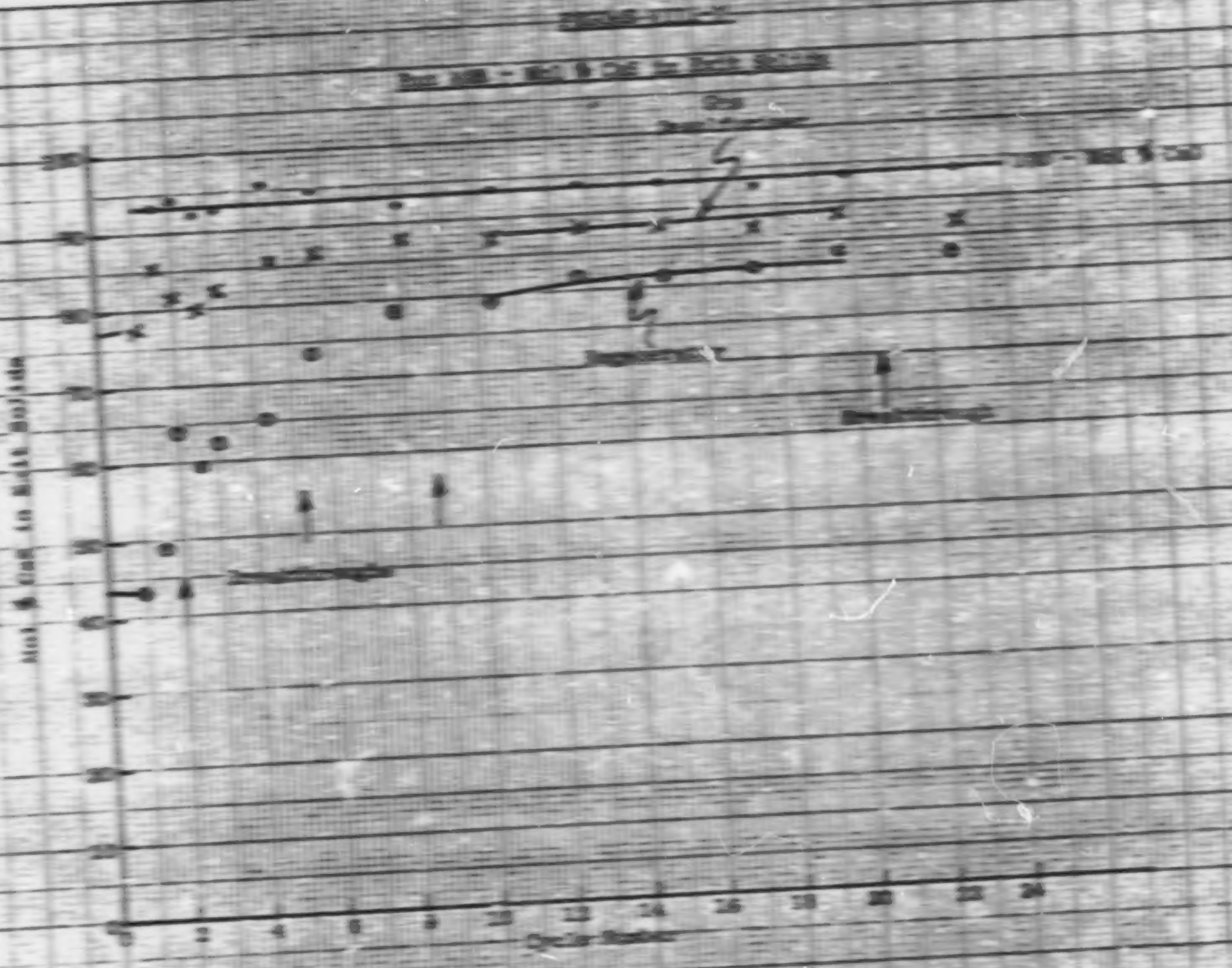
100
80
60
40
20
0
0
5
10
15
20
25
Cycle Number
Gas
Regenerator

FIGURE VIII-6

DEACTIVATION OF CaS WITH TEMPERATURE AS A PARAMETER




0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20


100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
14
16
18
20
22
24

Run A48 was made with Canaan stone which had been initially sulfided to a high conversion. This more closely simulated the conversion history of make-up stone fed to the process than did the technique of slowly building up the CaS content.

The run was started by sulfiding the stone batchwise at about 10%/hr for 7-1/2 hours. The combined sulfided product contained 78 mol % CaS. This was then fed to the unit continuously for regeneration. Some 40% of the CaS was converted to $CaCO_3$ leaving a CaS content of 47%. For the period encompassing the first regeneration through cycle 2.0, residence times were about 70 min in the gas desulfurizer and 80 min in the regenerator. For cycle 1-2, the stone was sulfided to 83% CaS and then regenerated to 49% CaS again yielding about 40% relative regeneration of CaS.

On the start of the third cycle (2-3), breakthrough occurred. A sample was not taken at this point, but the stone should have been about 98% CaS based on the H_2S feed rate. Upon breakthrough, the H_2S feed was reduced from 47 mol % of the calcium feed rate to 33%. The H_2S breakthrough disappeared and cycling continued. Breakthrough was again observed in cycle 5.3, and in cycle 5.6 the circulation rate was increased. This had the effect of reducing the sulfidation conversion to 13% of the calcium circulation rate and decreasing the residence time in each reactor to 40-50 minutes.

Upon further breakthroughs, the H_2S feed was reduced to give 8.8% and 4.0% sulfidation in cycles 8.9 and 10.0, respectively.

The H_2S content of gas leaving the desulfurizer was normally low during the course of the run except when insufficient $CaCO_3$ in the stone led to breakthrough. In Run A48 the $CaCO_3$ contents were: less than 8% on the first breakthrough, about 10% for the second, and less than 8% on the third and fourth breakthroughs.

It is believed that the higher $CaCO_3$ content at breakthrough observed early in the run was due to the high H_2S inlet rate. This is consistent with the assumption that breakthrough occurs at a constant space velocity of mols H_2S fed/hr:mole $CaCO_3$ in the bed.

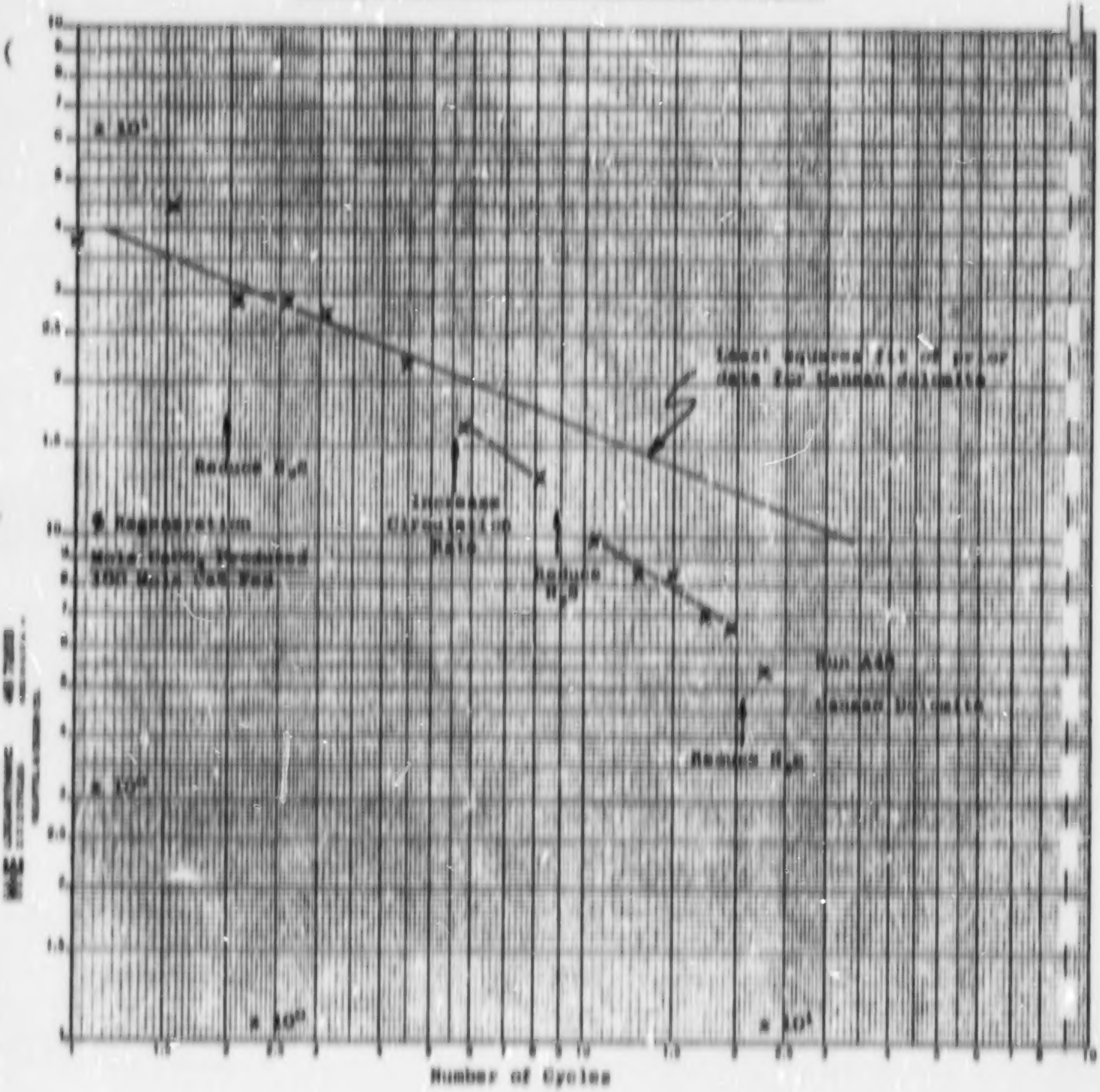
As shown in Figure VIII-8, the regeneration step was normal until the circulation rate was increased after the second breakthrough in cycle 5.6. From that point on, regeneration was worse than in previous runs with Canaan dolomite. For example, in cycle 10, the observed regeneration was 8.7% versus 18.0% expected. Based on previous experience, one would have expected a step drop in percent regeneration coincident with a step reduction in H_2S input or increase in circulation rate. The regeneration performance should then have remained constant for some time. In Run A48, there was no constant level of regeneration performance after the second and third breakthroughs. The data taken about the first breakthrough are inconclusive in this report.

The attrition rate observed was 0.9% which is lower than usual for Canaan dolomite.

In summary, the results of Run A48 differed from previous runs in that breakthrough occurred with more $CaCO_3$ present, regeneration was poorer, and the attrition rate was lower. In addition, reference to Figure VIII-18 (Section XVIII-D), which is a summary of density measurements on cycled Canaan dolomites, shows that the density of stone from Run A48 was higher than in previous runs.

FIGURE VIII-8

Run A48 - Deactivation of CaS at 704°C (1300°F)



The conditions for Run A48 differ in two respects from earlier runs; The stone was maintained at a high level of sulfidation from the very first cycle and the stone was exposed to gas desulfuriser conditions for some eight hours prior to its initial regeneration cycle followed by double the usual residence time in each vessel until cycle 8.8.

It is presumed that the longer desulfuriser residence times caused the stone to sinter during the cycling performance. At the conclusion of cycle 1, the density was consistent with that of earlier runs. The density increased markedly from cycle 1 to 10 and then increased slowly. The low attrition rate may be simply attributed to hardening and densification. The CaS in the unusually dense stone could have been less available for reaction thereby explaining the low regeneration activity.

C. Runs with Makeup

The objective of these runs was to more closely simulate proposed commercial operating conditions. More specifically it was desired to demonstrate that equilibrium activity of stone in a continuous make-up run can be calculated from runs where a single batch of stone was continuously cycled through the process.

Run A51

Run A51 was the first attempt to run with makeup. Due to an operating error, the sulfidation of the Canaan stone per cycle was only 15.3% on average. This was lower than intended, and the run was discontinued after 14 cycles. Detailed run results are presented in Tables VIII-1 and 2 and in Figure VIII-9. Except for the sulfidation conversion, the gas desulfuriser conditions were the same as for previous runs. In the regenerator, the recycle gas flow was increased in order to more closely approach equilibrium. A molar makeup of 4.8% fresh stone was fed to the gas desulfuriser.

The attrition rate and desulfurisation activity were satisfactory. The concentration of H_2S in the regenerator offgas reached 50% of equilibrium.

When using makeup, a regeneration-deactivation correlation cannot be made as it had been previously. Instead, various correlations are fitted to the data. For the makeup runs, three correlations, shown in Figure VIII-10, were used. These were:

a. The correlation based on previous runs with Canaan dolomite, excepting Run A48.

b. A correlation based on the deactivation data of Run A48.

c. An arbitrary intermediate correlation.

Application of these correlations to the actual conditions of Run A51, 4.8% makeup and 15.3% sulfidation, gave the results presented in Figure VIII-11. These results were obtained by inserting the run conditions into the computer program described in detail in Section VI. This program calculates the composition of an inventory of stone under given conditions of conversion, makeup rate, and deactivation behavior as a function of cycles. As the computer program for cycling does not take into account the presence

FIGURE VIII-9

Run A81 - Mol % CaO in Salt Solids

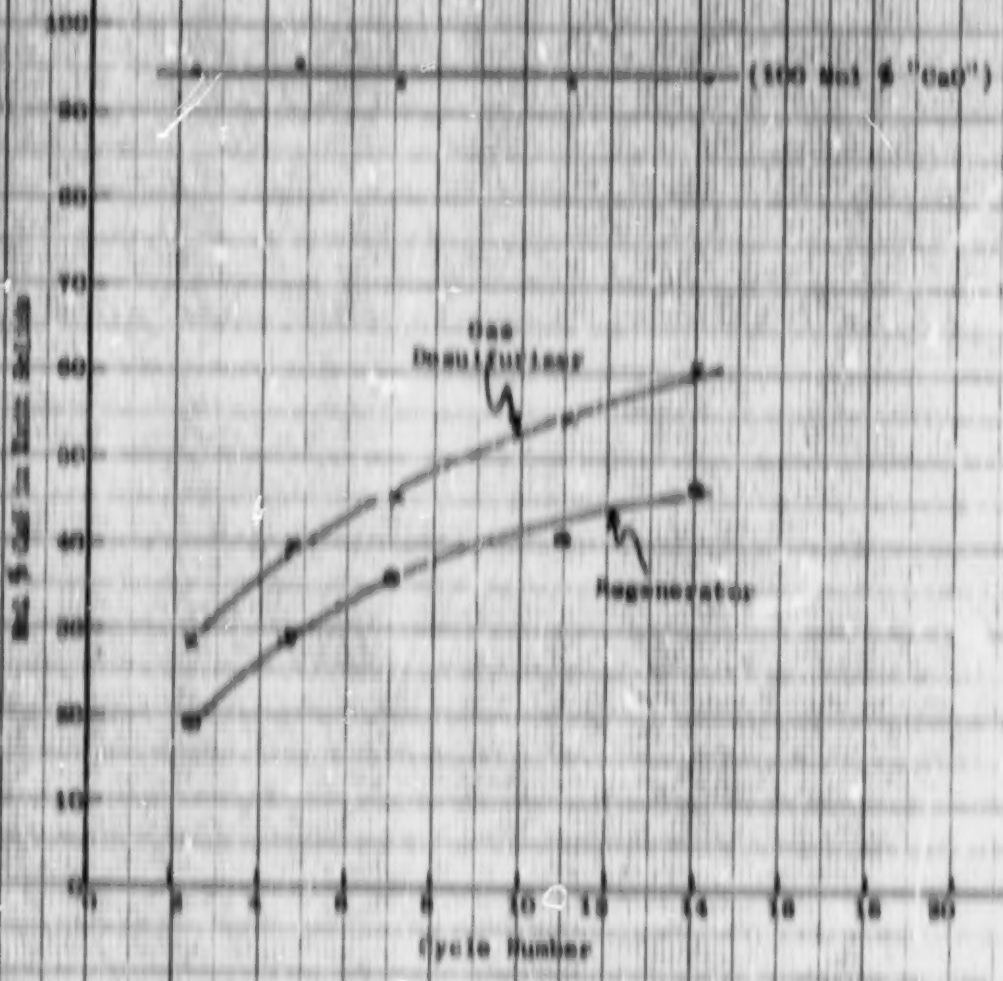
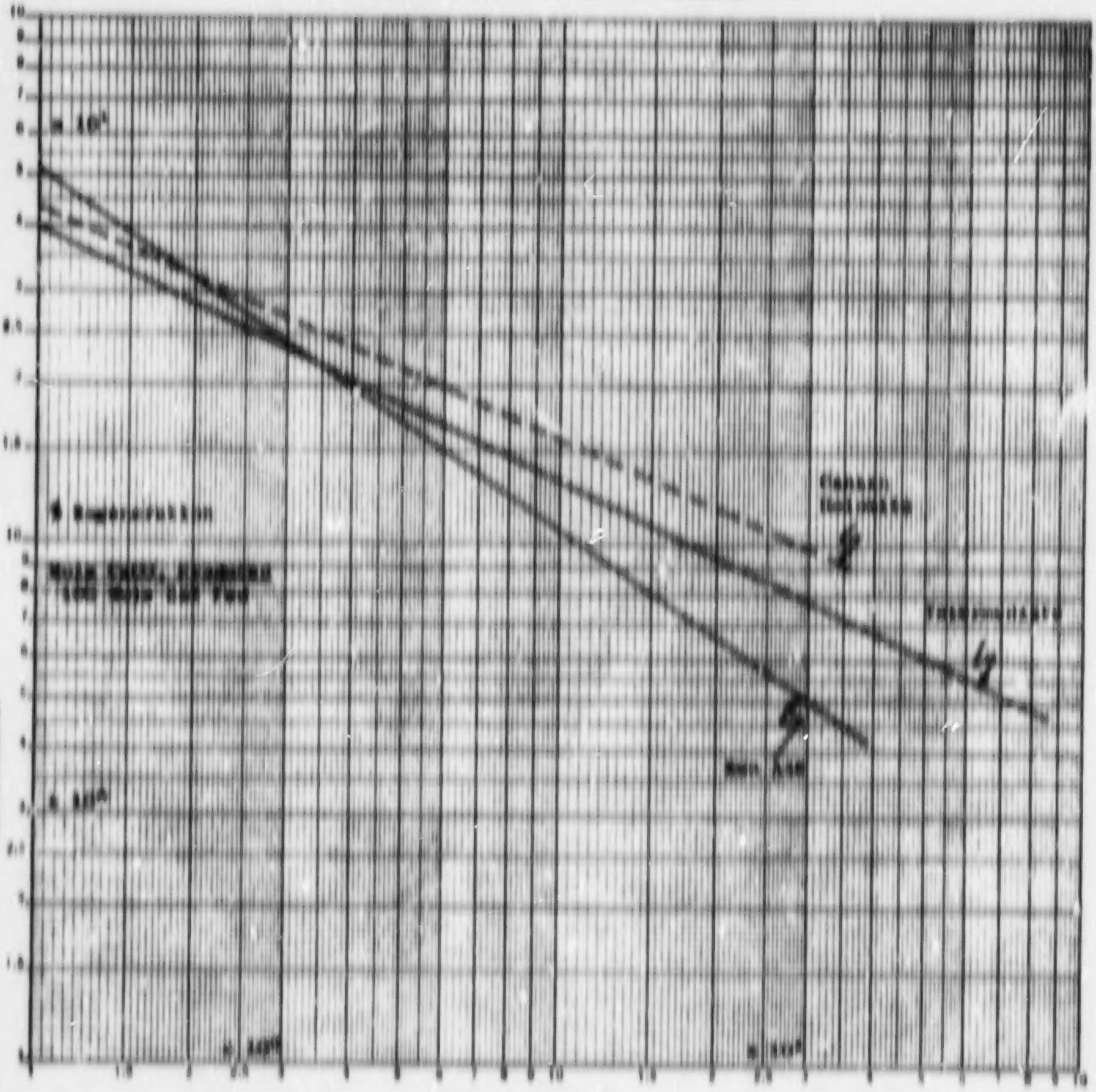
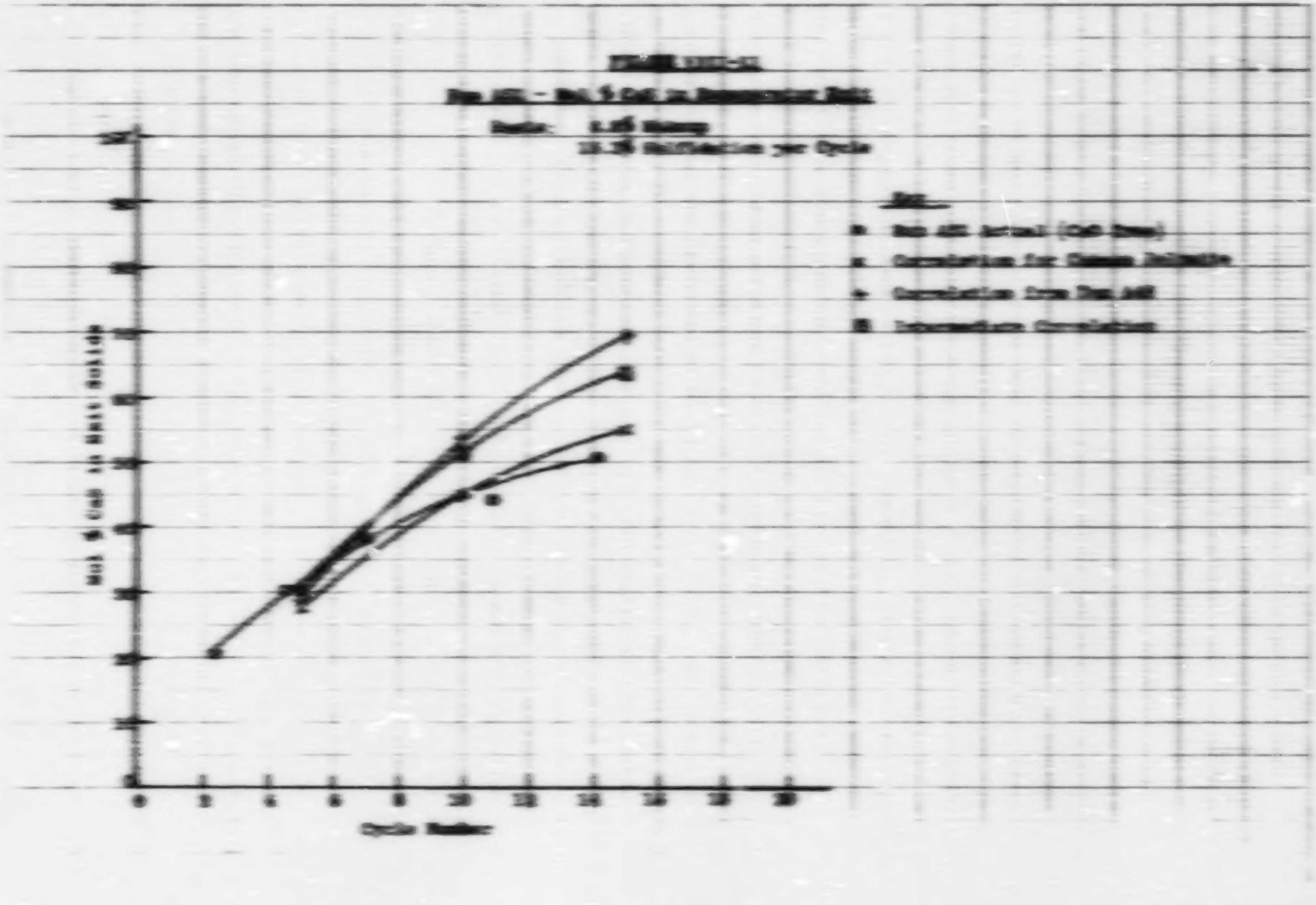


FIGURE VIII-10

Three Possible Correlations for Deactivation of CaO in Canaan Dolomite at 704°C (1300°F)




Scale:
per Cycle
Key:
Intermediate Correlation
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20
Cycle Number

of "CaO", the actual run data shown in Figure VIII-12 were put on a "CaO"-free basis. Figure VIII-11 clearly shows that the best fit is obtained with the Canaan data correlation.

Run A52A

The conditions for Run A52A were changed from Run A51 only by going to a sulfidation rate of 10.3% per cycle. The higher sulfidation level meant that the equilibrated CaS content leaving the gas desulfurizer would approximate proposed plant conditions. The make-up sorbent would be sulfided to a high conversion immediately, and there would be just enough excess $CaCO_3$ to prevent breakthrough. At a 5% make-up rate, the system would be 90% equilibrated with respect to CaS content in 40 cycles. The run lasted for 59 cycles. The only difficulty encountered was that the H_2S feed rate was low for cycles ca. 20-25. The raw run data on a "CaO"-free basis are plotted in Figures VIII-13 together with the three curves obtained from the trial correlations. The Canaan data correlation gives an excellent fit to the data, while the others clearly do not fit. In Figure VIII-14, results are shown for the inclusion of the temporarily lower H_2S feed rate in the computer input for the Canaan correlation. The fit of the Canaan correlation to the actual data was thereby improved.

The attrition rate was about 1%. Hydrogen sulfide concentration in the gas desulfurizer outlet was 0.01-0.03% until breakthrough. Breakthrough occurred with 4% $CaCO_3$ remaining. At 80% sulfidation, this is equivalent to a $CaCO_3$:H_2S molar space velocity of 3.5. For most of the run, the H_2S concentration in the regenerator was 60-75% of equilibrium. As in other tests, no deleterious effect of a high H_2S concentration on regeneration activity was observed.

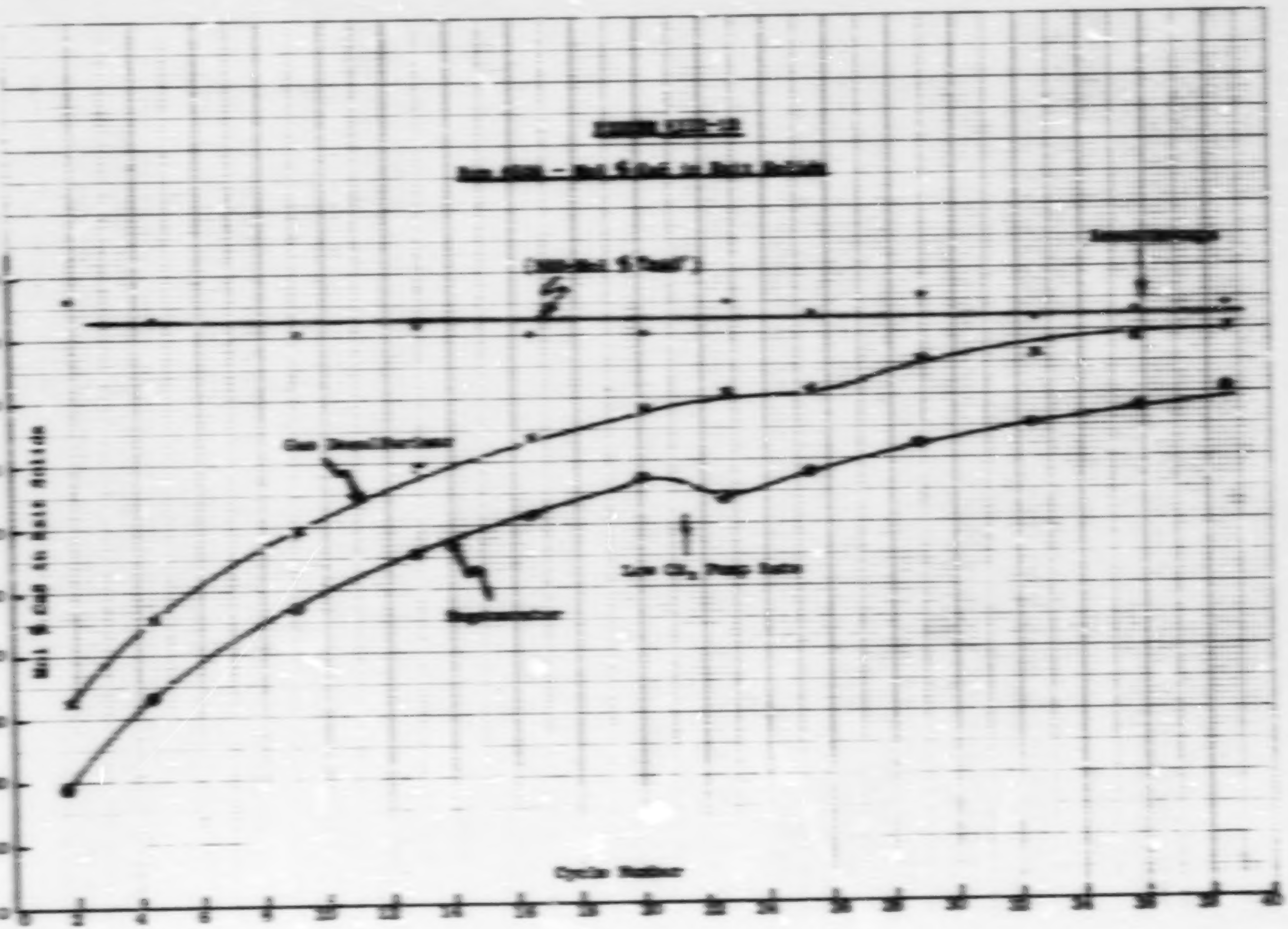
It is concluded that running with make-up acceptor to a high CaS level in the gas desulfurizer has no unpredicted effects on stone characteristics. The computer program for predicting activity of the inventory provided a good fit to the data.

D. Density Measurements on Cycled Canaan Dolomite

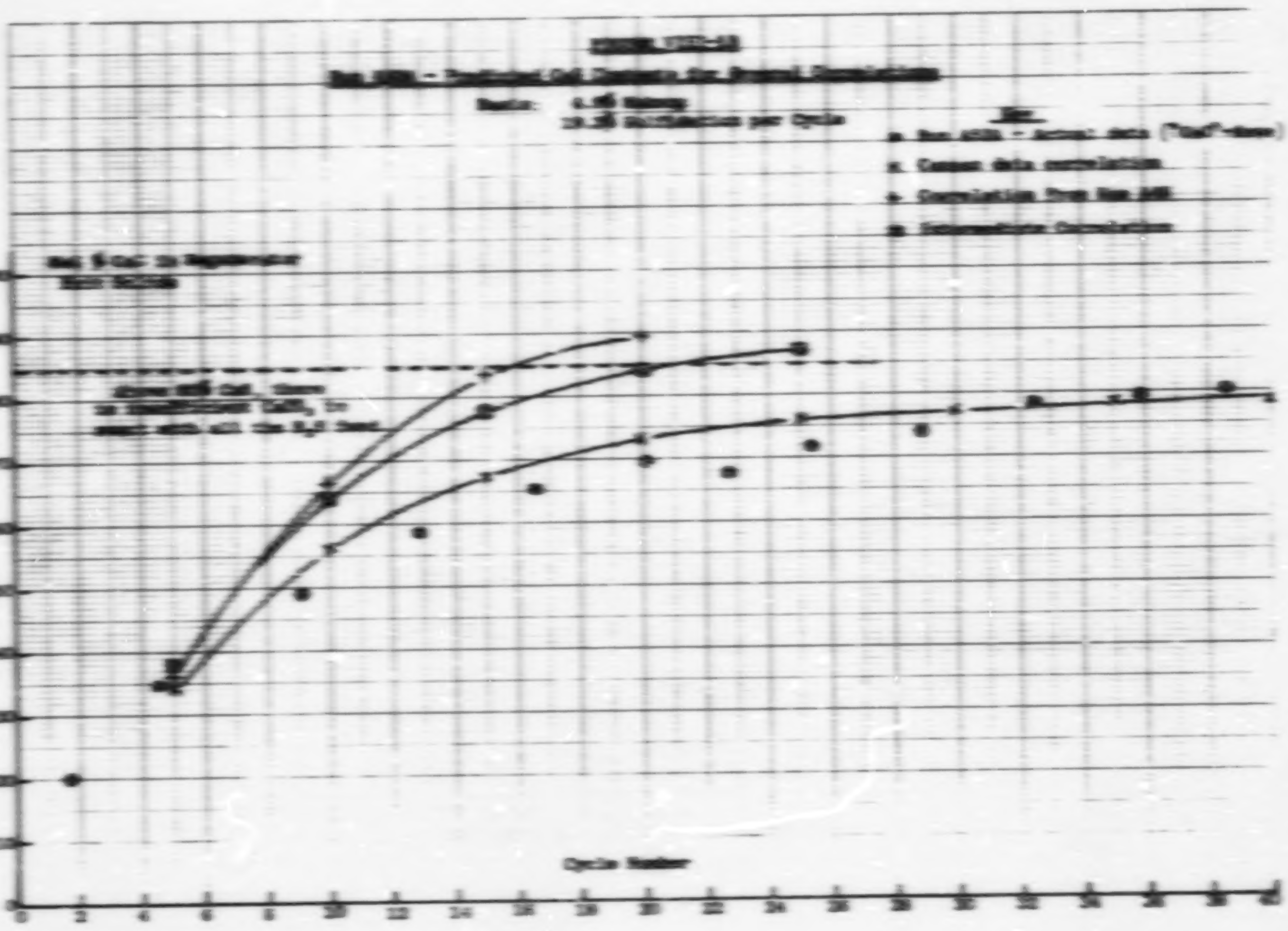
Density data for sulfided Canaan dolomites are presented in Table VIII-3 and in Figures VIII-15 and VIII-16. The data are normalized to a CaO·MgO basis in order to correct for the weight changes due to chemical reaction. In all cases, the density of the stone increased with cycling. There were differences between the runs: after 80 cycles, the stone from Run A48 had a normalized density of 123 lb/ft³ versus 99 lb/ft³ for the Run A51 stone. These represent the high and low ends of the density range.

Densification of stone probably occurs in the gas desulfurizer due to thermal sintering. As our experimental desulfurizer operated at 871°C (1600°F) instead of at 914°C (1678°F), the process design temperature, additional sintering would be expected at process conditions.

Runs A15, A50A and A52A were made at regenerator temperatures of 593, 704 and 760°C (1100, 1300 and 1400°F), respectively. Although the regeneration activity differed widely in these runs, Figure VIII-15 shows that the densities were the same. It is concluded that the regeneration temperature does not affect stone density.



Low CO₂ Pump Rate
Cycle Number
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40


Cycle Number
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
10
20
30
40
50
60
70
80
90
100

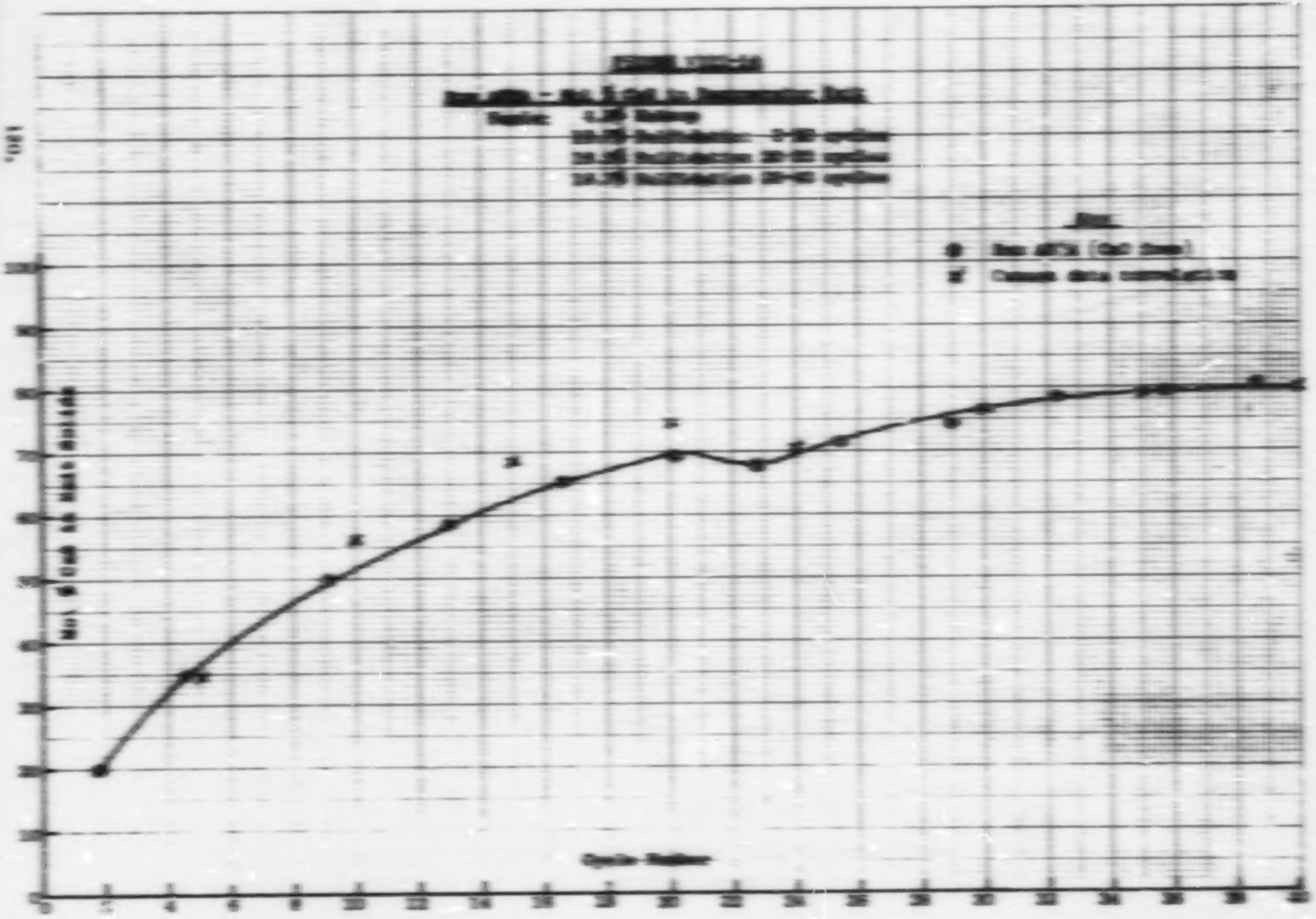
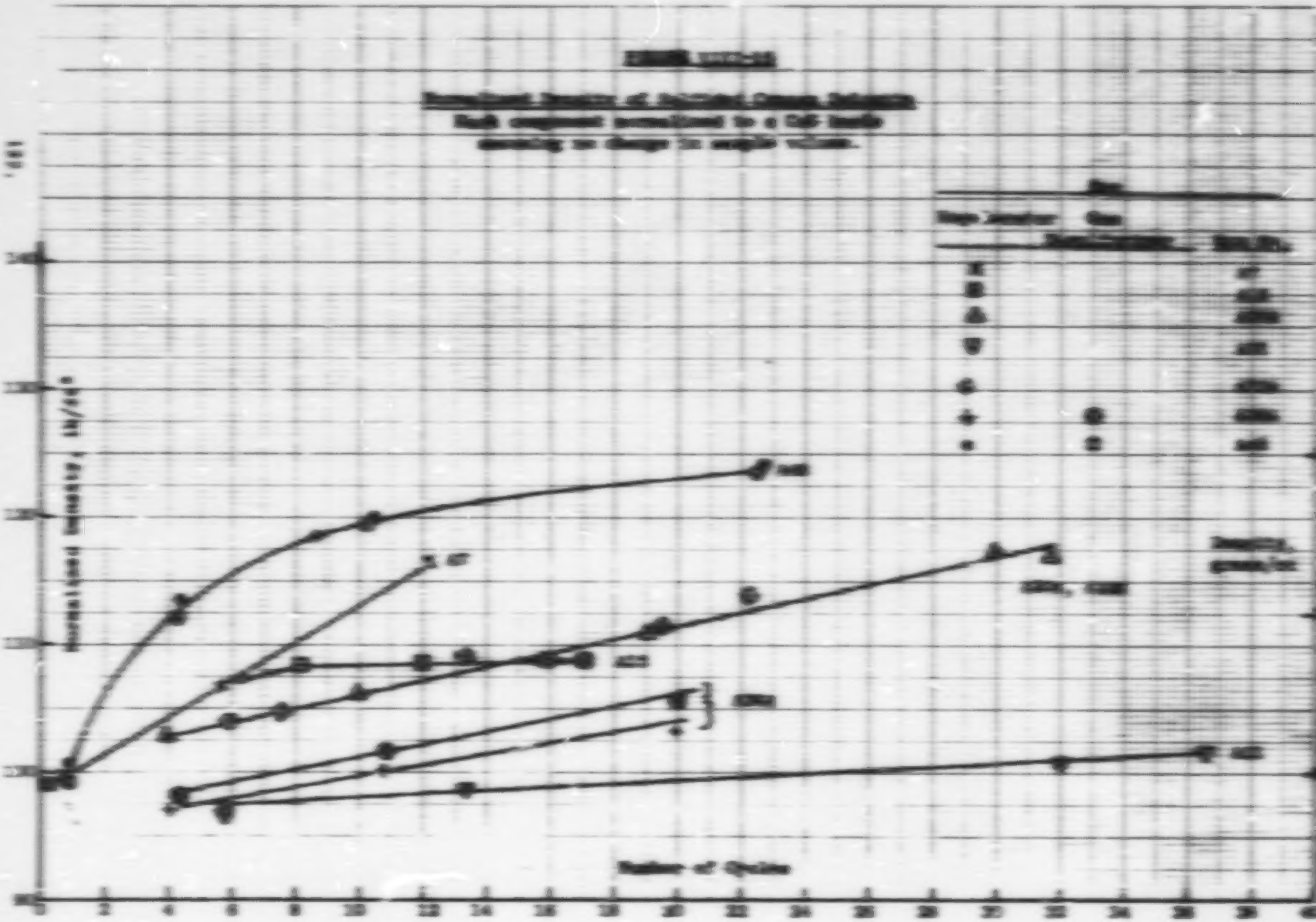

0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
100
200
300
400
500
600
700
800
900
1000

TABLE [illegible]

[illegible]

Run Number	Source of Sample	Cycle No.	Wt % of Total as [illegible]			Density(1)		Normalized Density(2)	
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A7	Gas Desulfurizer Regenerator	[illegible]	[illegible]	[illegible] (3)		[illegible]	[illegible]	[illegible]	[illegible]
A16	Regenerator	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
A18	Regenerator	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
A20A	Regenerator	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A21	Regenerator	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A22A	Regenerator	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A23A	Gas Desulfurizer Regenerator	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A26	Gas Desulfurizer Regenerator	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A31	Regenerator Gas Desulfurizer	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A32A	Regenerator	[illegible] (4)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

(1) Measured by mercury at 1 atmosphere.
(2) Calculated by normalizing each calcium component to a CaO basis while assuming no change in sample volume.
(3) For these samples, [illegible] was determined by [illegible], and CaS was estimated as the difference from 100 wt %.
(4) Note: This is not the same as cycles in a run without makeup. When using makeup, the average age of the stone is less than the number of cycles.


each component normalized to a [illegible] basis
assuming no change in sample volume.
Normalized Density
Number of Cycles
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
Density, grams/cc

All the runs with Canaan dolomite gave low attrition rates, but the more dense stones generally exhibited lower attrition rates. The overall attrition rate for Run A48 was 0.3% versus 0.8% for Run A51.

The cause of the variation in densities is not yet known. The high densities observed in Run A48 may have been due to the protracted initial residence time in the gas desulfurizer. The low densities observed in Run A51 are more difficult to explain. The only variable change was the use of extra recycle gas in the regenerator which increased the H_2S concentration. It is thought that the H_2S concentration may affect the crystal morphology thereby influencing the degree of densification which later occurs in the desulfurizer. The evidence for this occurring in our system is rather indirect, and the model is discussed more fully in Section XV.

For Runs A51 and A55A, normalized density as a function of cycles is shown in Figure VIII-16. The data are on the high side of the range of densities reported for other Canaan dolomite runs. It is noted that after 40 cycles the arithmetic average age weighted for the quantity of stone was about 17 cycles. The equilibrium average age would be 19.5 cycles. At the end of Run A55A, the normalized density was 1.84 gm/cc (115 lb/ft³). The corresponding numbers for Runs A51, A50A, and A48 were: 1.59, 1.76 and 2.00 gm/cc (99, 110 and 125 lb/ft³), respectively.

E. Attrition Data

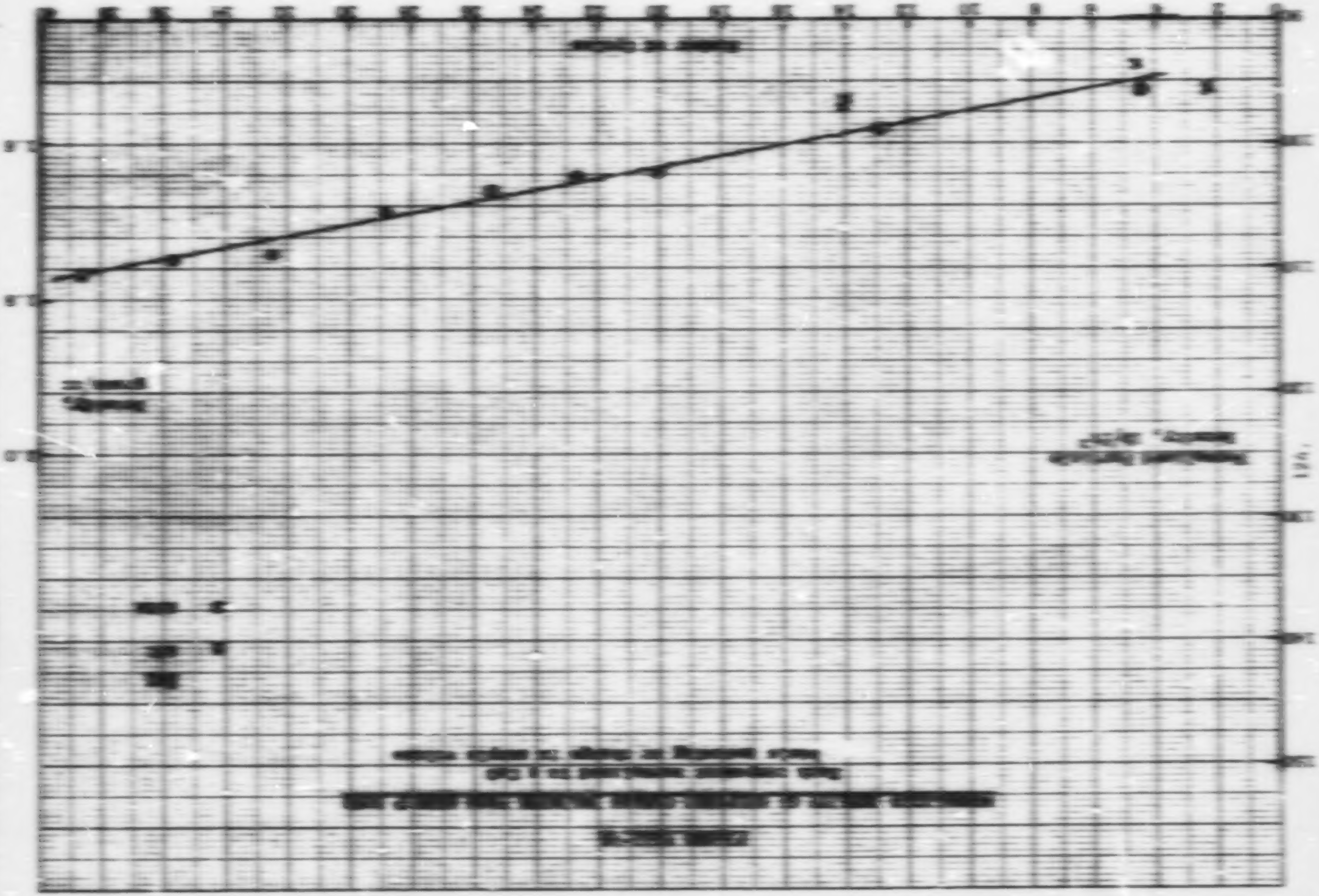
Attrition data as a function of cycles are presented in Figure VIII-17. The attrition rate was consistently under 1%. In four out of five cases, the observed rate of attrition decreased as cycling continued. It is assumed that this is due to sintering and densification of the stone as indicated by the increase in normalized density. Run A51 was the only one which showed a leveling trend in attrition as it was cycled, and this run showed the least densification.

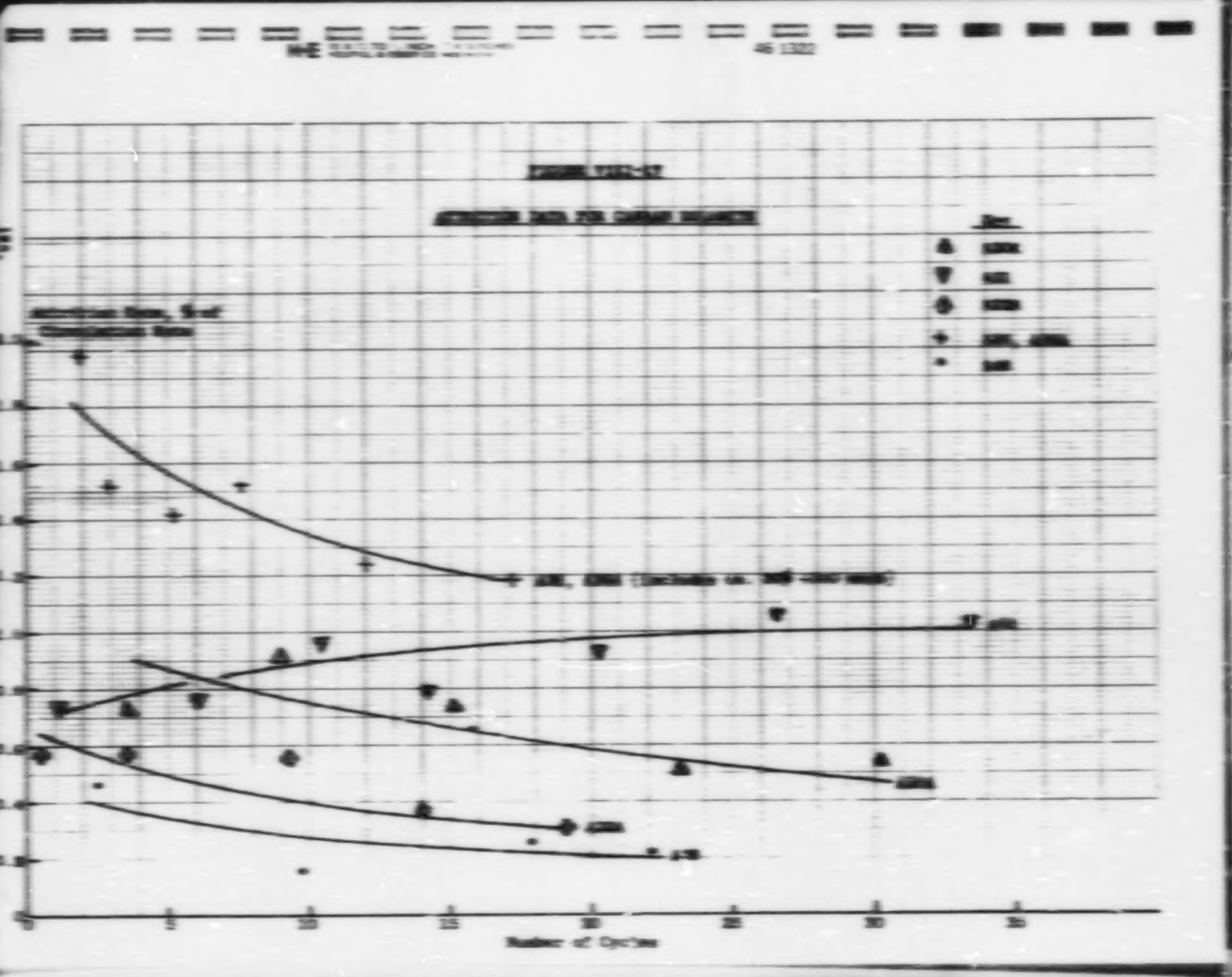
Attrition results for runs with makeup are given in Figure VIII-18. For these runs, there is an increase in attrition followed by a decrease. The normalized density showed a steady increase. It is noted that the recycle runs and Run A51 shared the condition of a high H_2S concentration in the regenerator, and the result of an attrition rate which initially increased and then leveled off or decreased. It is thought that the H_2S effect may have been responsible for the observed effects via its influence on crystal morphology. However, a detailed model of the mechanism has not been formulated.

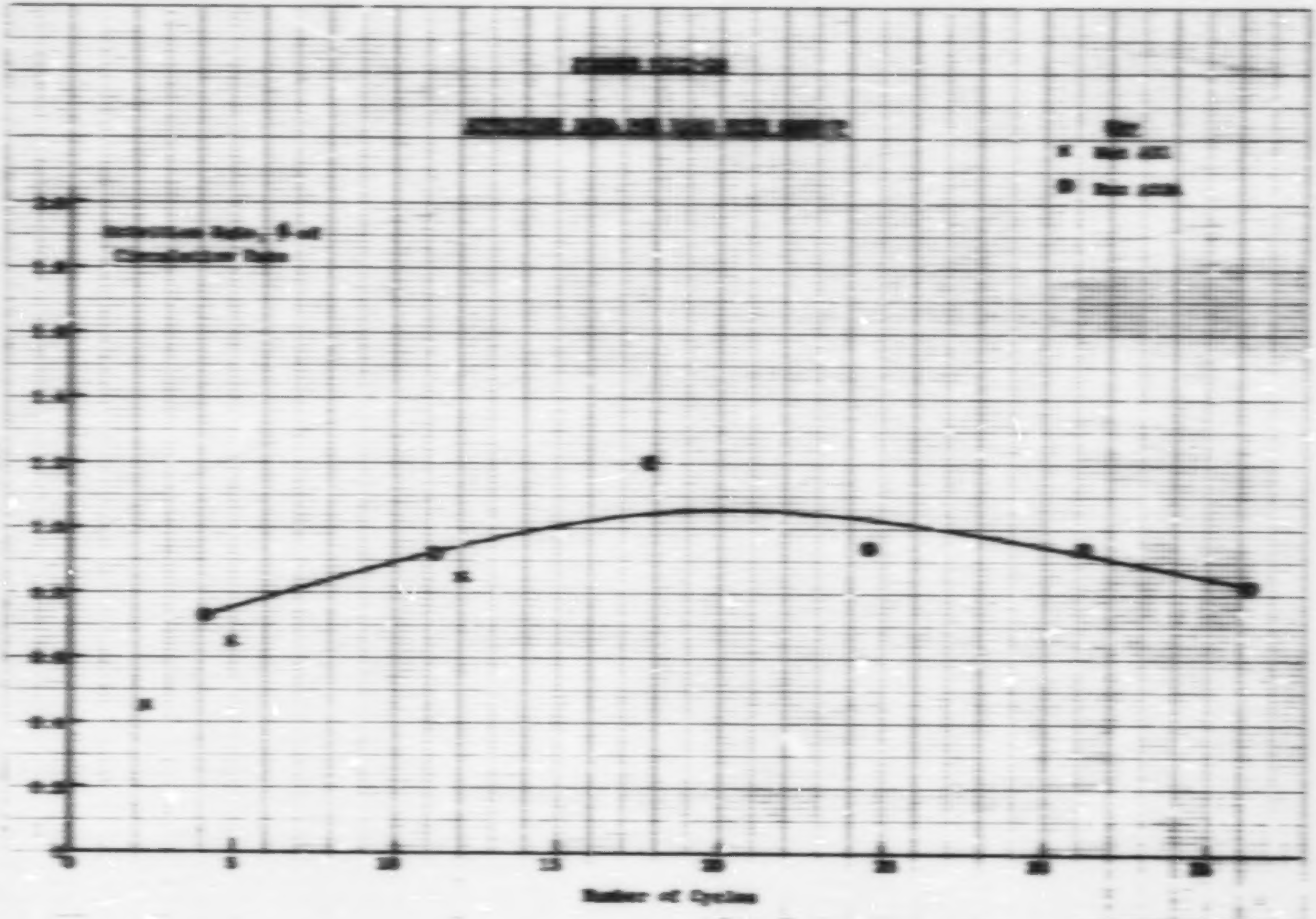
F. Conclusions

The key conclusion is that, experimentally, Canaan dolomite exhibits the characteristics required to fit into the process design presented in Section III. Specifically, the following were shown to be true:

1. The gas desulfurizer can be operated without breakthrough until most of the $CaCO_3$ is consumed. This is true even when the stone has undergone numerous cycles.




46 1322
0
5
10
15
20
25
30
35
Number of Cycles


0
5
10
15
20
25
30
35
Number of Cycles

2. The decline in regeneration activity is sufficiently slow to enable the stone to be recycled for a large number of cycles. A low make-up rate can therefore be used.

3. There is no influence of a high H_2S concentration on the rate of regeneration under our conditions. It should therefore be possible to run at a high H_2S concentration in the regenerator offgas and also to maintain the required regeneration rate.

4. The attrition rate is on the order of 1%. This is less than the required make-up rate to maintain activity.

5. The activity of an acceptor inventory obtained in a system using makeup can be calculated from non-makeup run data. Thus, the results of simple cycling runs can be used for process design calculations.

IX. CYCLIC CONTINUOUS RUNS WITH HARDENED DOLOMITES

A. Introduction

In the previous study,(1) three of the four dolomites tested displayed high rates of attrition. These were Tymochtee, Buchanan and Pennsylvania dolomites. It was decided that a method of hardening local dolomites was needed for those cases where a local hard stone of good activity was not available.

Work on the CO_2 Acceptor Process(11) had shown that Tymochtee dolomite was initially soft in the $CaCO_3$-CaO cyclic process. However, the stone hardened in that cycle when fuels containing sulfur were used. It was determined that $CaSO_4$ was involved in producing a transient liquid phase which helped the stone become attrition resistant. Attrition rates of less than 1.0% were observed in both bench-scale(11) and the pilot plant units.

With this background information, it was decided to harden the stone in our desulfurization process via an oxidation step involving formation of $CaSO_4$.

B. Batch Hardening Tests

Exploratory batch runs were made with Tymochtee dolomite to harden the stone via formation of low-melting liquids in the system $CaSO_4$-CaS-$CaCO_3$. Tests were run batchwise using the gas desulfurizer reactor. The stone was first sulfided at 871°C (1600°F) according to the conditions given in Table IX-1 and then oxidized according to the conditions given in Table IX-2. The planned procedure was to sulfide the stone to about 70 mol % CaS and then oxidize all the CaS to $CaSO_4$. Using this procedure a wide range of compositions from 0-70-30 to 70-0-30 molar $CaSO_4$-CaS-$CaCO_3$ would be obtained. As a final step the $CaSO_4$ was reduced back to CaS.

In Run HR1, air was fed at a rate sufficient to oxidize the stone within two hours. However, a severe exotherm developed and the run was shut down when the observed temperature exceeded 1040°C. Runs HR2 and HR3 were made at much lower air rates and the temperature was readily controlled at 871°C (1600°F) and 927°C (1700°F), respectively. The HR1 product formed an agglomerated mass in the vessel but the HR2 and HR3 products were free flowing.

Products were tested for attrition resistance in two ways. The first was to put a screened sample on a rolling mill under controlled conditions and then rescreen it. Results of these tests for the exploratory runs and for several standards are given in Table IX-3. The HR1 product was considerably better than A2 product, a sulfided Tymochtee dolomite, and not quite as hard as Run A20 product, a sulfided Canaan dolomite. However, Run HR2 and HR3 products were still about the same as unhardened stone. In the table, all stones are compared to A8, a Tymochtee product first hardened in the CO_2 Acceptor Process cycles and then tested in the present sulfiding-regeneration cycle.(1)

The other method of checking strength was to screen out a 28 x 48 Tyler mesh fraction, and perform a drop test on a small sample with the apparatus shown earlier in Figure IV-3. The resulting material was then screened for over and under 48 mesh weights. Results given in Table IX-4 were in agreement with the results of the rolling mill test.

TABLE IX-1

Conditions for Batchwise Dolomite Sulfiding

System Pressure: 15 atm (206 psig)
System Temperature: 871°C (1600°F)

Run Number	HR1	HR2	HR3	HR4 to HR10
Acceptor	← Tymochtee Dolomite →			
Size Consist, Tyler Mesh	← 28 x 48 →			
Sulfiding Time, min	← 270 →			
Input, SCFH[1]				
Recycle to Bed	← 145 →			
H_2S	← 1.58 →			
CO_2	← 8.8 →			
H_2	← 25.0 →			
H_2O	← 21.4 →			
N_2	← 66 →			
CO	← 23.0 →			
Purges (N_2) above Bed	← 15 →			
Recycle Lift Gas (only for feeding)	← 70 →			
Fluidizing Velocity, ft/sec	← 0.42 →			
Total Amount of Acceptor Fed, grams	2800	3400	2800	2800
Total Amount of Sulfur Fed, gram mole	← 6.35 →			

(1) Input is given after shift reaction and hydrolysis of CS_2 have taken place.

TABLE IX-2

Conditions for Batchwise Oxidation of Sulfided Dolomite

System Pressure: 15 atm (206 psig)

Run Number	HR1	HR2	HR3	HR4 to HR10
Acceptor	Sulfided Tymochtee Dolomite			
Oxidizing Time, hours	ca .75[1]	53.75	28	9
Temperature, °C	(2)	871 (1600°F)	927 (1700°F)	982 (1800°F)
Input, SCFH				
Recycle to Bed	← 138 →			
Air	55	9	9	8
CO_2	70	90	90	88
N_2	--	108	105	90
Purges (N_2) above Bed	← 15 →			
Total Amount of O_2 Fed in Air, gram mole O_2 (till breakthrough)	N.D.[1]	16.7	14.3	11

(1) Air was on and off in efforts to control temperature.
(2) Uncontrollable due to agglomeration, max. temperature > 1040°C.

[illegible]

[illegible]

[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	—	—	—	—	—	—	—	—	[illegible]
[illegible]	[illegible]	[illegible]	—	—	—	—	—	—	—	[illegible]
[illegible]	[illegible]	[illegible]	—	—	—	—	—	—	—	[illegible]
[illegible]	[illegible]	[illegible]	—	—	—	—	—	—	—	[illegible]
[illegible]	[illegible]									
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]					[illegible]
[illegible]										
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	—	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]									
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]									
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

(1) [illegible]

(2) [illegible]

(3) [illegible]

[illegible]

[illegible]

[illegible]		[illegible]				[illegible]		[illegible]		[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] [illegible]	[illegible] [illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] [illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	—	—	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible] [illegible] [illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

(1) [illegible]

(2) [illegible]

TABLE IX-4

Results of Drop Tests
Samples: 0.50 gm
Drop Height: 6.3 cm

Feed was 35 x 48 mesh
Product was screened at 48 mesh

Test Material	Average % Undersized Material, 3 or More Drops	Average Absolute Deviation
A3GA Final Regenerator Bed	13.5	2.6
A3 Final Regenerator Bed	27.7	3.5
HR1 Product	20.7	1.3
HR2 Product	27.3	5.1
HR3 Product	30.8	1.5
HR4 Half-Calcined	35.0	1.4
HR4 Sulfided	32.9	1.9
HR4 Oxidized	26.5	2.0
HR4 Reduced	31.8	1.1
HR5 to HR10 Composite	26.6	3.2

Hardening Run HR4 was made at the conditions shown in Tables IX-1 and IX-2. The oxidation step was carried out at 982°C (1800°F) and lasted about nine hours as compared to about 30 hours in Runs HR2 and HR3. Oxidation was followed by a one hour reduction at the same conditions shown in Table IX-1, except that no H_2S was fed. In Run HR4 samples were taken in the course of the run so that changes in the stone could be followed as processing continued.

Some agglomerates were formed during the run. Examination of the product under a microscope showed a surface which appeared to have gone through a liquid stage, i.e., the overall particle shape was retained but the surface had been smoothed. Products of Runs HR1, HR2 and HR3 had a similar appearance.

As shown by the rolling mill test data in Table IX-3, HR4 product had indeed been hardened. The drop test data of Table IX-4 do not show much improvement in hardness. As the HR4 stone was later shown to actually be attrition resistant, the drop hardness test was no longer used.

Table IX-3 contains data on stone composition and density as it passed through the hardening process. The density data are presented on a normalized basis which takes into account the effect of molecular weight changes on density as discussed in Section VI. In the series HR1 to HR4, the lowest density is associated with half-calcined stone. The products oxidized at 982°C (1800°F) are most dense followed by the 927 and the 871°C products. In addition, the data for HR4 show a steady increase in density in going through the transformations from half-calcined to sulfided to oxidized to the reduced state.

It is noted that the level of $CaCO_3$ increased in going from the sulfided to the oxidized state and again in going from the oxidized to the reduced form. $CaCO_3$ can be formed from CaO and CO_2 following disproportionation of $CaSO_4$ and CaS as well as from CaS by the action of H_2O and CO_2.

Run AS2

While the hardening step at 982°C (1800°F) suffered from potential operability problems, a feedstock for a continuous sulfiding-regeneration run was made up in order to quickly determine whether the stone was actually attrition resistant and to get feedback on the activity of $CaCO_3$ and CaS in the gas desulfurizer and regenerator, respectively. Five batches, Runs HR5 to HR10 were made at the same conditions as HR4. In four of these runs, there was evidence of agglomeration. A total of 680 grams of +28 mesh agglomerates were formed for about 8000 grams of free flowing -28 mesh stone.

Continuous run conditions were chosen to correspond to Run AS1, except for the use of less recycle gas in the regenerator for the first few cycles. This was because the feed contained sufficient active CaS to possibly cause the early regeneration to be equilibrium limited. Conditions and results from the gas desulfurizer and regenerator are given in Tables IX-5 and IX-6, respectively. Detailed data on solids composition, H_2S content of dry exit gas, and attrition as functions of cycle number are presented in Appendix B for all runs in this chapter.

From 0 to 3.9 cycles, recycle to the regenerator was kept low (35 SCFH) in order to prevent the possible large initial regeneration of the heavily CaS-laden stone from being limited by equilibrium. From 3.9 to 10.5 cycles, a recycle flow of 108 SCFH was maintained in order to closely approach the design value of 67% approach to equilibrium.

Breakthrough of H_2S in the gas desulfurizer occurred at 10.8 cycles. At this point, it was decided to increase the solids circulation rate by about 80%. This reduced the absolute conversion of Ca per cycle, and should have enabled the regenerator to lower the CaS level and thereby relieve breakthrough. Upon increasing the circulation rate, the H_2S content of the regenerator offgas started to rise. The maximum observed was 4.00% via the U.V. analyzer and 4.35% via G.C. analysis (dry basis). This was substantially the equilibrium H_2S concentration. Since the regeneration was now equilibrium limited, the recycle flow was returned to its original level of 35 SCFH at 10.3 cycles in order to lower the H_2S concentration in the regenerator offgas.

After the circulation rate was increased, the H_2S concentration in the gas desulfurizer exit gas fell from 0.13% to 0.08%. The regeneration activity of the stone was then so low that breakthrough increased, and the run was shutdown.

Figure IX-1 shows the CaS content of solids as the run progressed. Figure IX-2 plots the regeneration activity of the solids. The raw activity data do not fall on a single line. However, by displacing each point 3 cycles, a single line can be drawn through the scattered points. It is reasonable that some deactivation occurred due to the sulfidation, oxidation, and reduction which were carried out prior to the cyclic run. The data indicate that the hardened stone deactivated more rapidly than fresh Canaan dolomite. The rapid deactivation accounts for the lack of success in totally relieving breakthrough by increasing the circulation rate. The stone just did not retain enough regeneration activity to raise the $CaCO_3$ level enough to eliminate breakthrough.

The results of the run indicate that increasing the circulation rate is a good method of reducing breakthrough. It has potential as a means of controlling sulfur absorption in a plant.

A highly significant result of A33 was the substantial attainment of equilibrium in the regenerator.

It is difficult to pin down the exact percent approach to equilibrium. The inaccuracies of the factors which go into such a calculation must be taken into account. These are the following: H_2S and CO_2 concentrations in the exit gas, steam flow rate, exit gas flow rate, temperature at the top of the bed, and the accuracy of the equilibrium constant itself. All things considered, the observed value of 99% is a close approximation of 100% of equilibrium. It is noted that the process design assumes only 88% approach.

The attrition rate was quite low, 0.35% of the circulation rate over the entire run. The run demonstrated that the hardening procedure was effective in producing an attrition resistant stone albeit at the cost of reduced activity. The very low attrition rate indicated that the hardening procedure was overdone. Run A34 was made at only 30% sulfidation in the hope that the attrition rate would still be less than 1% and that activity would be improved.

C. Continuously Hardened Tymochtee 10 Dolomite

Run A34

The hardening conditions for Run A34 were 30% sulfidation followed by oxidation at 982°C (1800°F). Each step was carried out continuously at the

[illegible]

[illegible]

[illegible]

[illegible]

[1] [illegible]

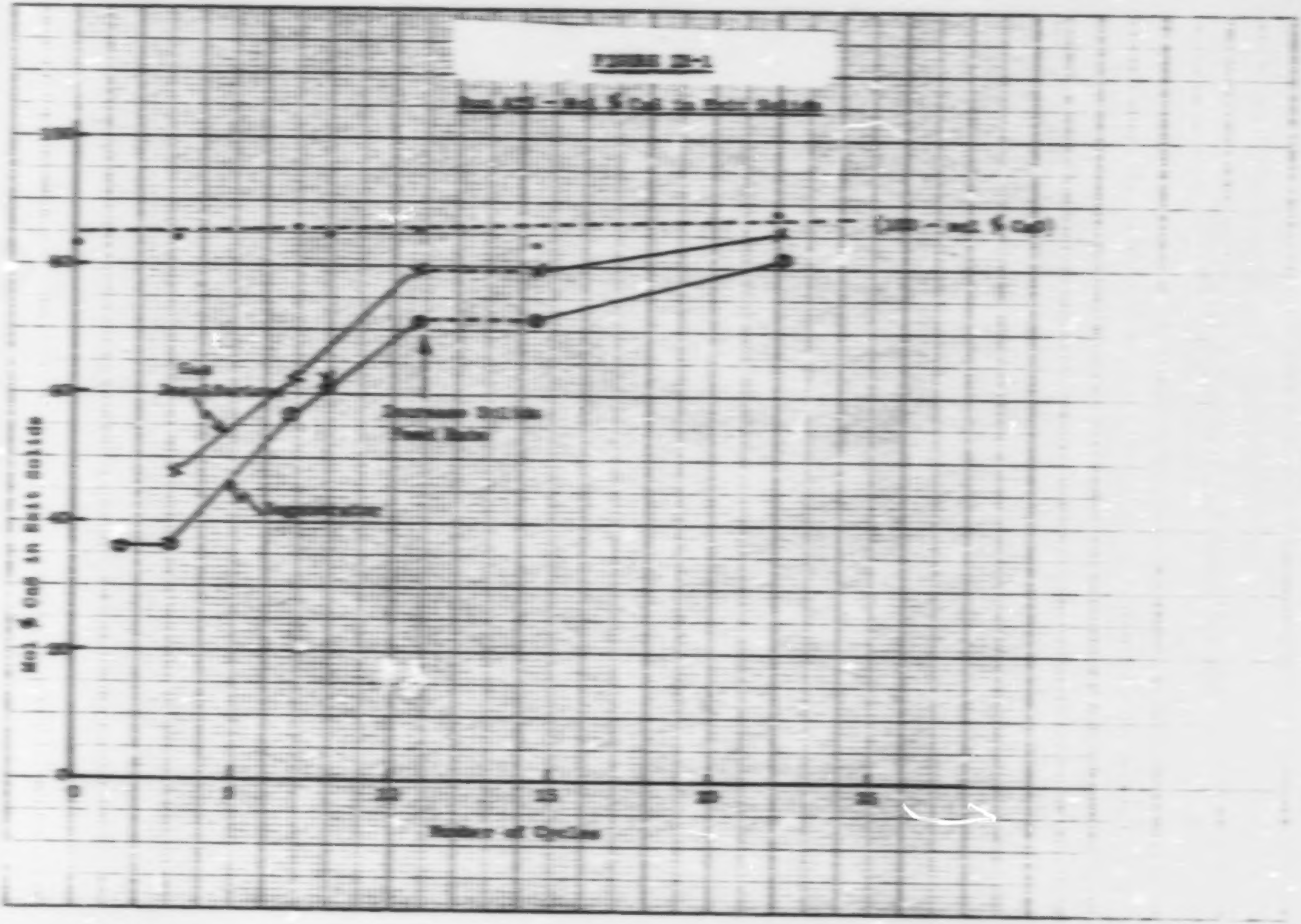
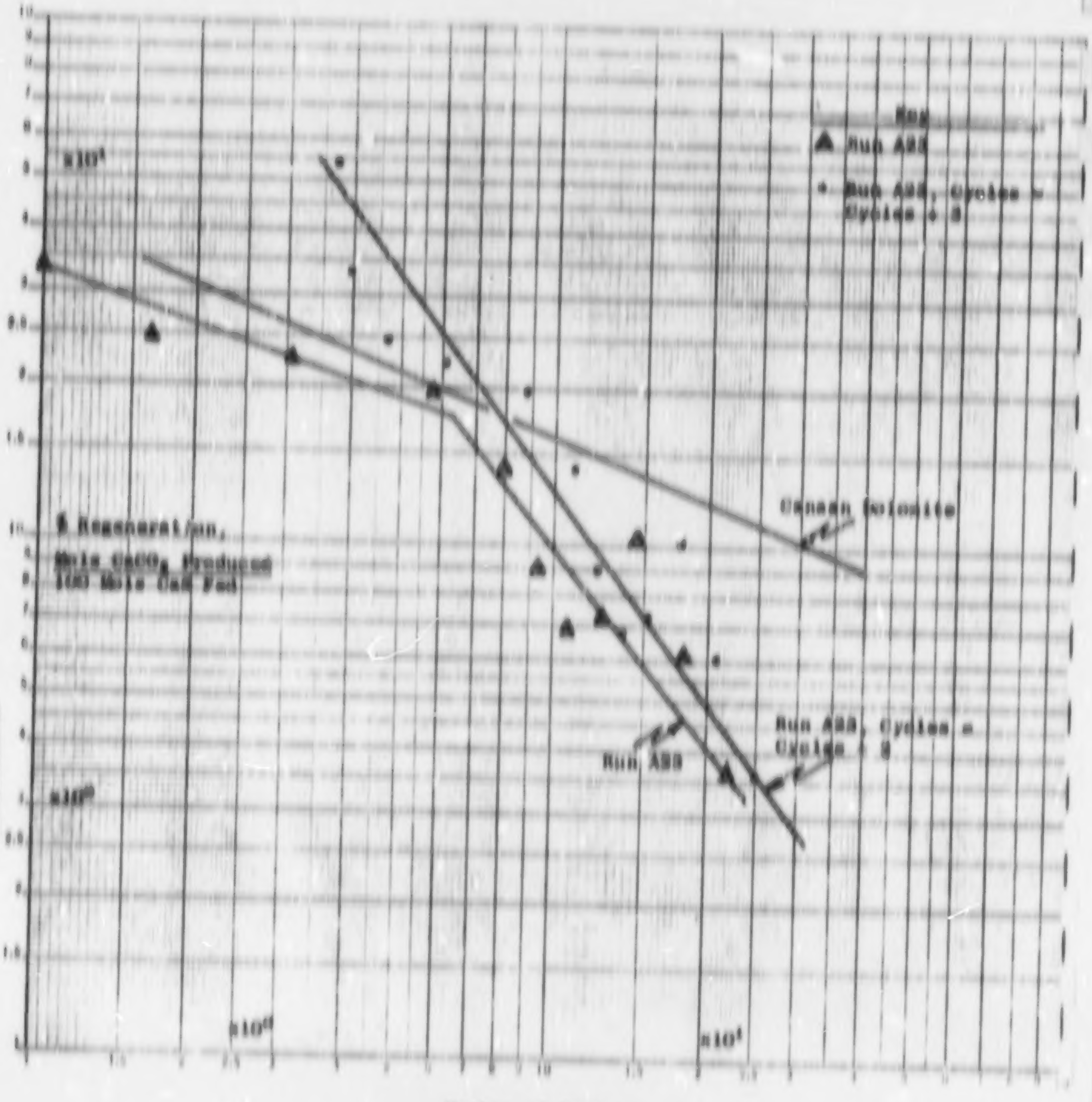


FIGURE [illegible]

Run [illegible] - Mol % CaO in Bath Solids

FIGURE IX-9

Run A23 - Deactivation of CaS at 704°C (1300°F)



conditions shown in Tables IX-7 and IX-8. Reduction of $CaSO_4$ was carried out simultaneously with the first sulfidation of the run's cyclic phase. There was no evidence of agglomeration or operability problems in the hardening step.

For the cyclic part of the run, a modest recycle flow of 35 SCFH was used in the regenerator since the feasibility of approaching equilibrium had already been demonstrated. Analysis of solids showed that over 90% of the $CaSO_4$ was reduced in the gas desulfurizer in the first cycle. The $CaSO_4$ content was zero within a few cycles. This result is consistent with the earlier batch data obtained when the reduction was run separately.

Regeneration activity was better than in Run A23 and, after 13 cycles, the CaS content of solids leaving the gas desulfurizer was still under 70 mol %. In order to examine the behavior of the stone at breakthrough, the CS_2 (H_2S) feed rate was doubled at cycle 13.4 until breakthrough at cycle 14.6. The CS_2 was then reduced to its original value of ca. 13 mol % per cycle. When the CS_2 was cut back, the H_2S concentration in the exit fell from 0.34% to 0.04%. After about an hour, it rose to 0.08%. Unfortunately, the inventory of acceptor was too low to allow an increase in circulation rate and the run was shutdown. The progress of the run as defined by the CaS content of the solids is presented in Figure IX-3.

The attrition rate for Run A24 was 0.77%, well within the goal of 1% or less. The regeneration activity was better than in Run A23. The data plotted in Figure IX-4 indicate that activity was nearly the same as for Canaan dolomite. Thus, a hardened acceptor was produced with no penalty in activity.

Run A25

The hardening conditions for Run A25 were 80% sulfidation followed by oxidation at 927°C (1700°F). As in Run A24, the hardening was carried out continuously and reduction took place during the run.

Regeneration activity was better than in Run A24 and, after 13 cycles, the CaS content of solids leaving the gas desulfurizer was under 60%. In order to examine the behavior of the stone at breakthrough, the CS_2 feed rate was doubled from cycle 13.4 until breakthrough at cycle 16.1. The CS_2 pump setting was then cut back to its original value, and the H_2S fell from 0.3% to 0.03% at the gas desulfurizer exit. A second breakthrough did not occur and, after making a sulfur balance, it was concluded that the pump malfunctioned so that the molar CS_2 feed was on the order of 5-6% rather than 13% of the calcium circulation rate. The run was continued to 30 cycles to gain appreciation of the long term regeneration behavior.

The CaS content of the solids versus cycles is shown in Figure IX-5. The regeneration activity shown in Figure IX-6 was slightly better than that of Canaan dolomite. The attrition rate was an acceptable 0.74% of the circulation rate.

After Run A25, a calibrated CS_2 reservoir was installed so that the actual delivered volume could be continually monitored.

TABLE [illegible]

[illegible]

Run Number	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Acceptor Size Fraction, Tyler mesh	[illegible] x [illegible] →						
Feed Rate, gm/hr [lbs/hr]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Reactor Solids Residence Time, min.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Input, SCFH[1]							
Recycle to bed	[illegible] →						
H_2O	21.4 →						
H_2	[illegible] →						
CO	[illegible] →						
CO_2	[illegible] →						
N_2	[illegible] →						
H_2S	[illegible] →					[illegible]	[illegible]
Purges (CH_4) to bed	[illegible] →						
Purges (N_2) above bed	[illegible] →						
Recycle Acceptor Lift Gas, above bed	[illegible] →						

[1] Input is given after shift reaction and hydrolysis of CO_2 have taken place.

Run Number	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Acceptor Size Fraction, Tyler mesh	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] →		
Feed Rate, gm/hr [lbs/hr]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Reactor Solids Residence Time, min.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible][1]	[illegible]
Input, SCFH[2]							
Recycle to bed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H_2O	[illegible]	[illegible]	21.4	[illegible]	21.4	[illegible]	21.4
H_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H_2S	[illegible] →					[illegible]	[illegible]
Purges (CH_4) to bed	[illegible] →						
Purges (N_2) above bed	[illegible] →						
Recycle Acceptor Lift Gas, above bed	[illegible] →						

[1] [illegible]

[2] Input is given after shift reaction and hydrolysis of CO_2 have taken place.

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]														
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

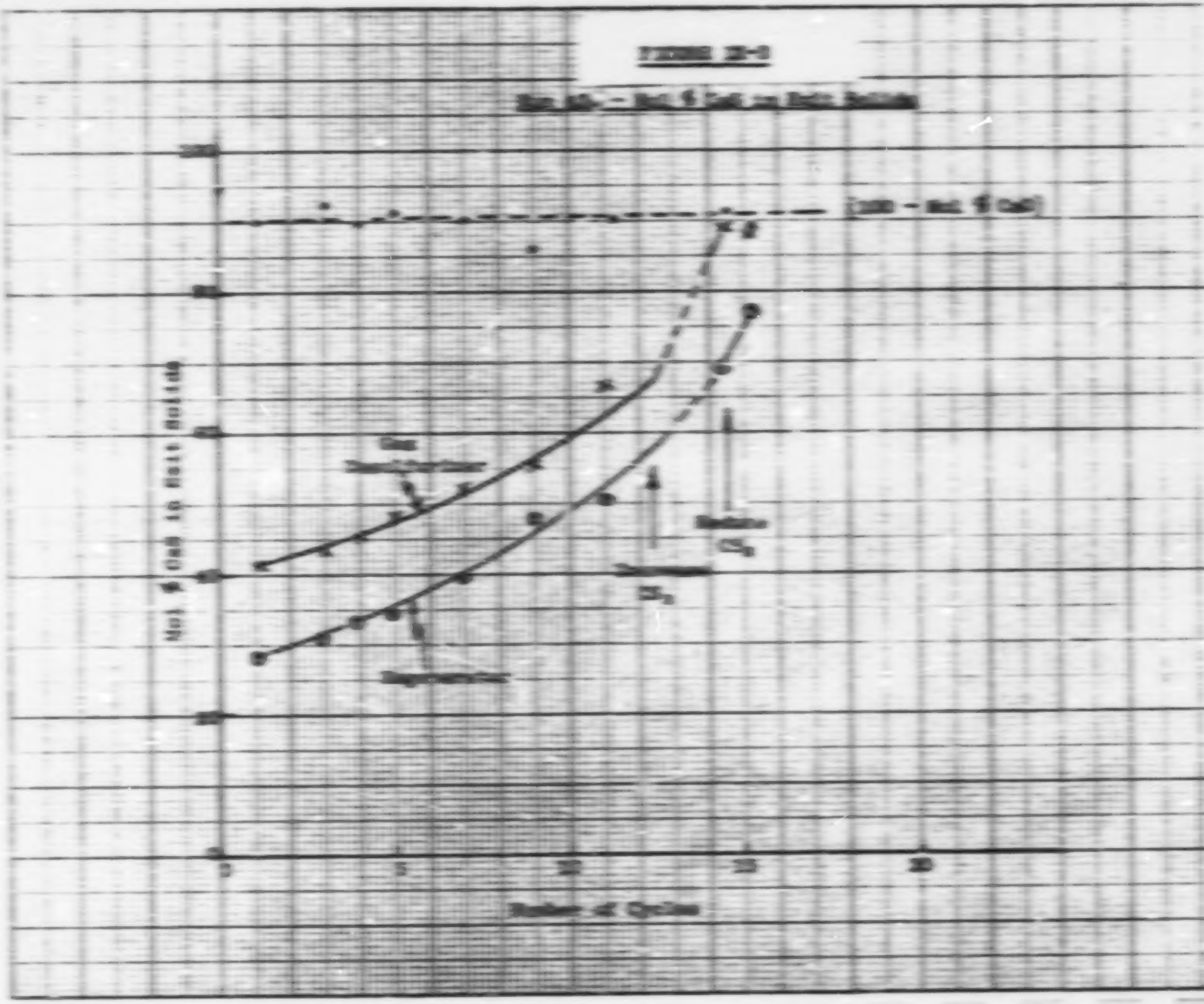

[illegible]
Mol % CaO in Melt Solids
Number of Cycles
0
5
10
15
20
Regeneration

FIGURE IX-4

Run A24 - Deactivation of CaO at 704°C (1300°F)

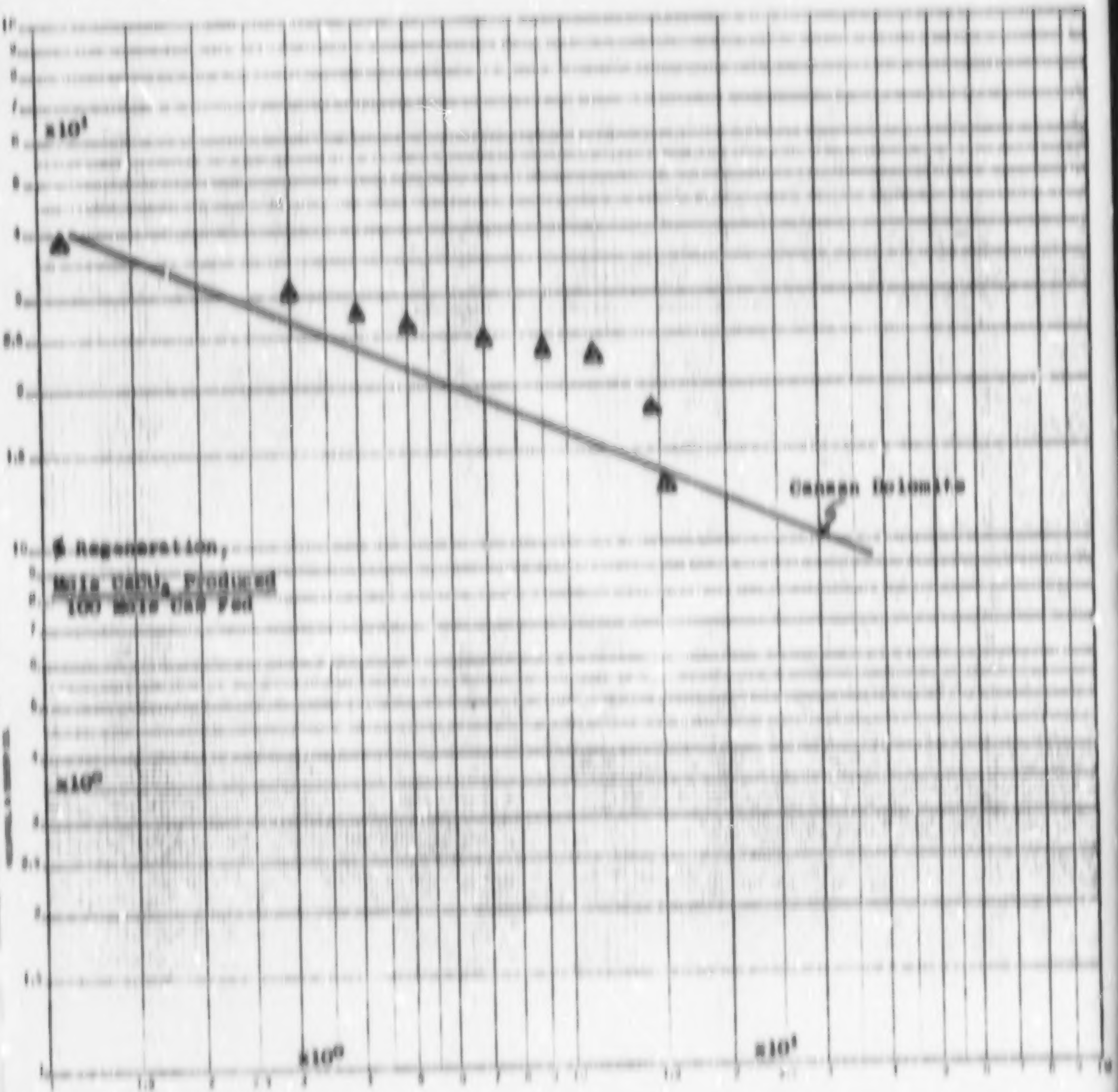
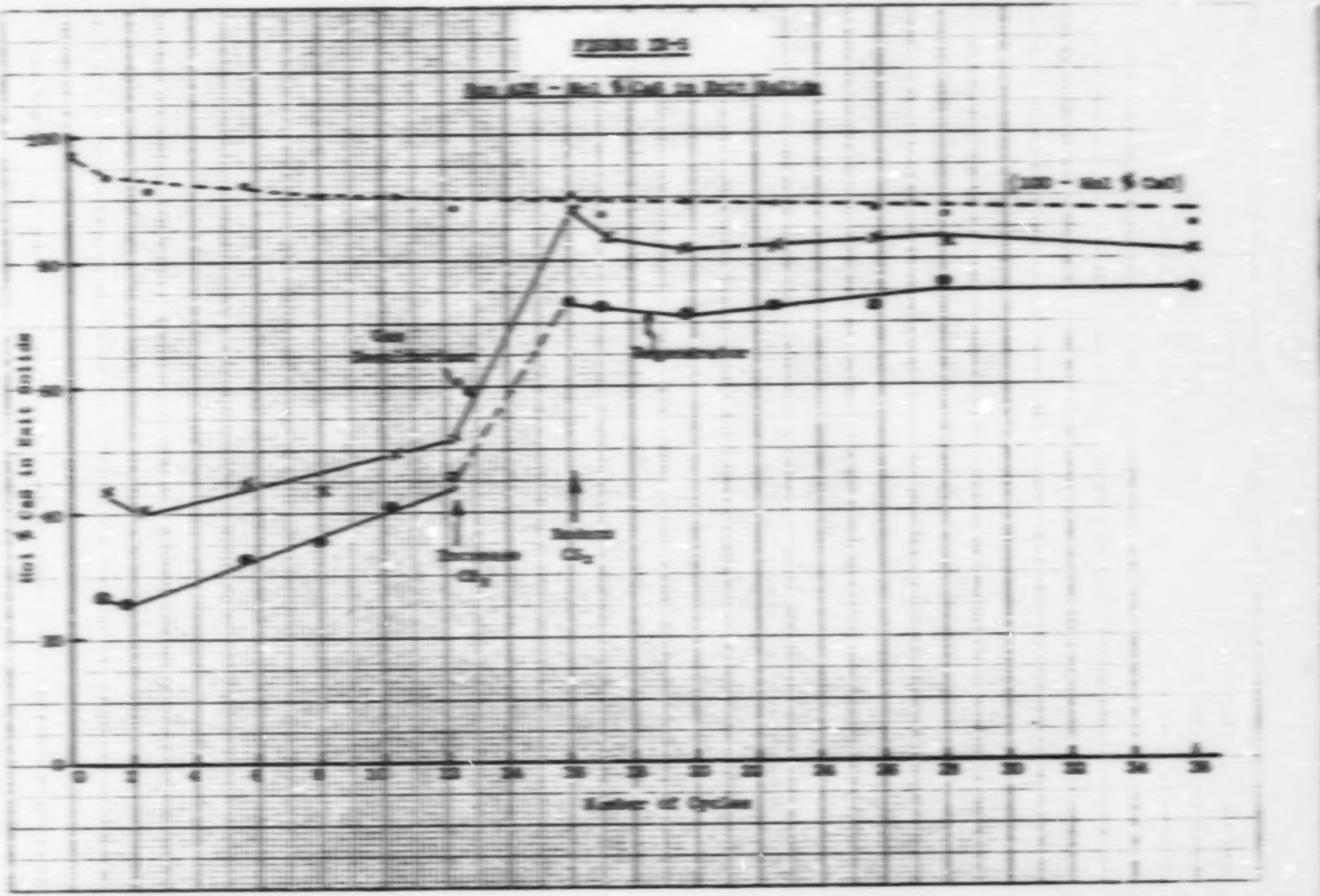


FIGURE [illegible]

[illegible] - Wt % Cat in Exit Solids



Run A26

The feed for Run A26 was prepared via sulfidation to 25 mol % CaS at 871°C (1600°F) followed by oxidation at 899°C (1650°F). The attrition rate of the cyclic run was 0.6% of the feed rate, and the deactivation behavior of the stone was the same as for Run A25. The run was terminated when breakthrough occurred. About 4 mol % of $CaCO_3$ remained in the stone at the time of breakthrough. The run data are presented graphically in Figures IX-7 and IX-6.

Run A27

The feed for Run A27 was prepared via sulfidation to 20 mol % CaS at 871°C (1600°F) followed by oxidation at the same temperature. The attrition rate remained low, 0.7%, and the activity was satisfactory. The run data are summarized in Figures IX-8 and IX-6. The run was continued until breakthrough occurred at which time the $CaCO_3$ content of the stone was ca. 1-2%.

Run A28

The temperature of 871°C (1600°F) was compatible with other process flows, and it was felt that there was little to be gained by lowering the temperature of the hardening process any further. Consequently, reduction of the initial sulfiding level was explored. For the Run A28 hardening step, both the sulfidation and oxidation were carried out at 871°C (1600°F) at a molar conversion of 10% of the calcium.

The attrition rate of the cyclic phase was 0.7%, and the activity was normal. The run was terminated after 10 cycles; the concentrations of CaS during the run are given in Figure IX-9.

Figure IX-6 represents all the regeneration data for runs in which the feed was hardened over the temperature range of 871 to 927°C (1600-1700°F) and 20-30% sulfidation. The results of the four runs are consistent, and display an activity slightly better than that of Canaan dolomite. The attrition rate was less than 1% for all of the above runs.

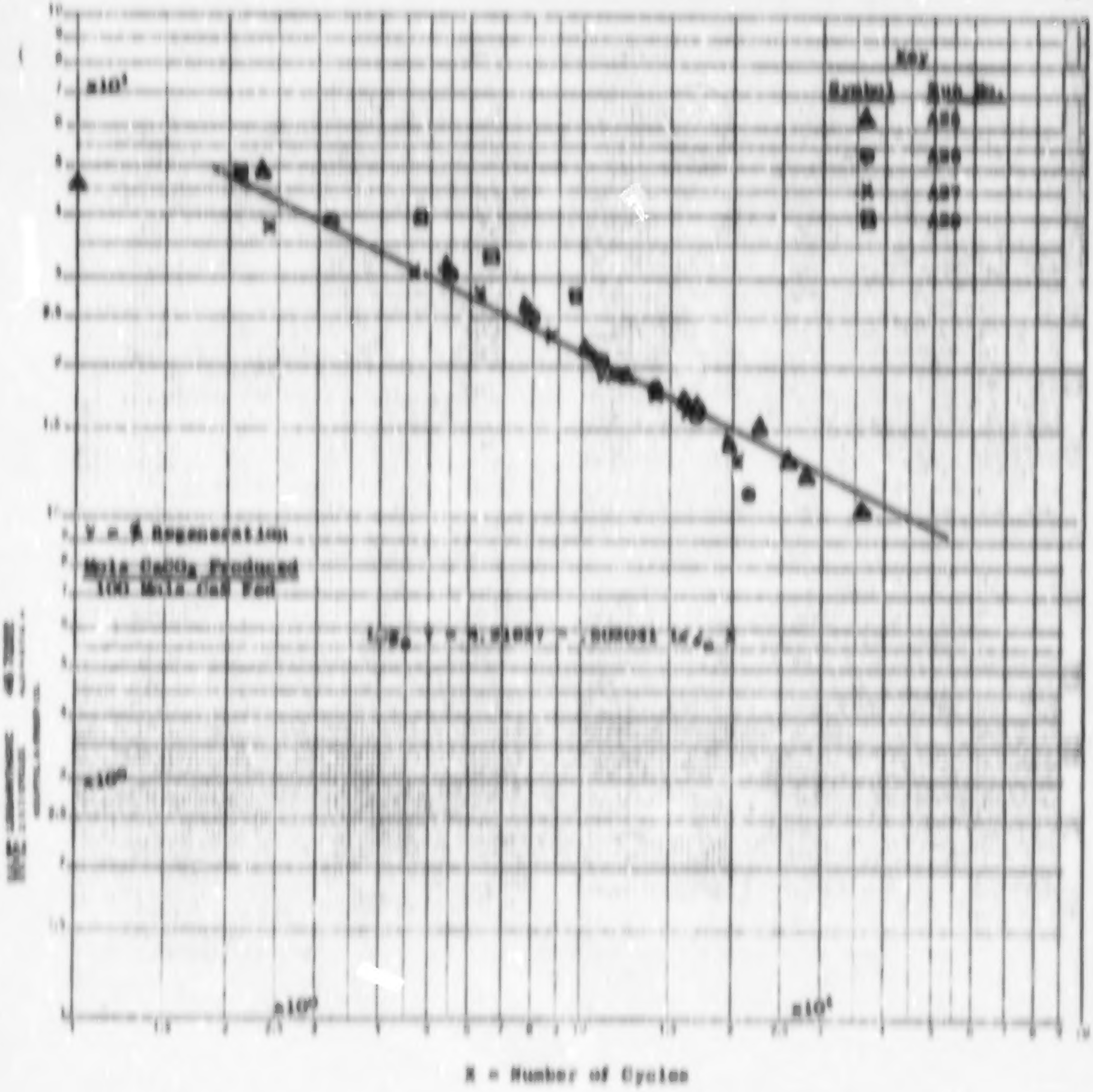
Run A29

The preparation of Run A29 feed was run at 4.4% sulfidation. This is the same level which was used in Run A4(1) when oxidation of 4 mol % of the calcium was performed at 704°C (1300°F) in each cycle. No hardening was observed in Run A4. The attrition rate observed in the cyclic phase of Run A29 was 1.1% for cycles 0-4.8. By the period 4.8-7.2 cycles, the attrition rate had fallen to 0.7%. As shown in Figure IX-11, the regeneration behavior was better than that of hardened Tymochtee 10 dolomite. The run was ended after 7 cycles (Figure IX-10).

The data indicate that 4% sulfidation followed by oxidation is not sufficient to produce a feedstock which will immediately have an attrition rate of less than 1%. However, the behavior of the A29 feed was curious in that the attrition rate steadily decreased. Therefore, a run was made in which the hardening operation lacked the addition of H_2S in the first step.

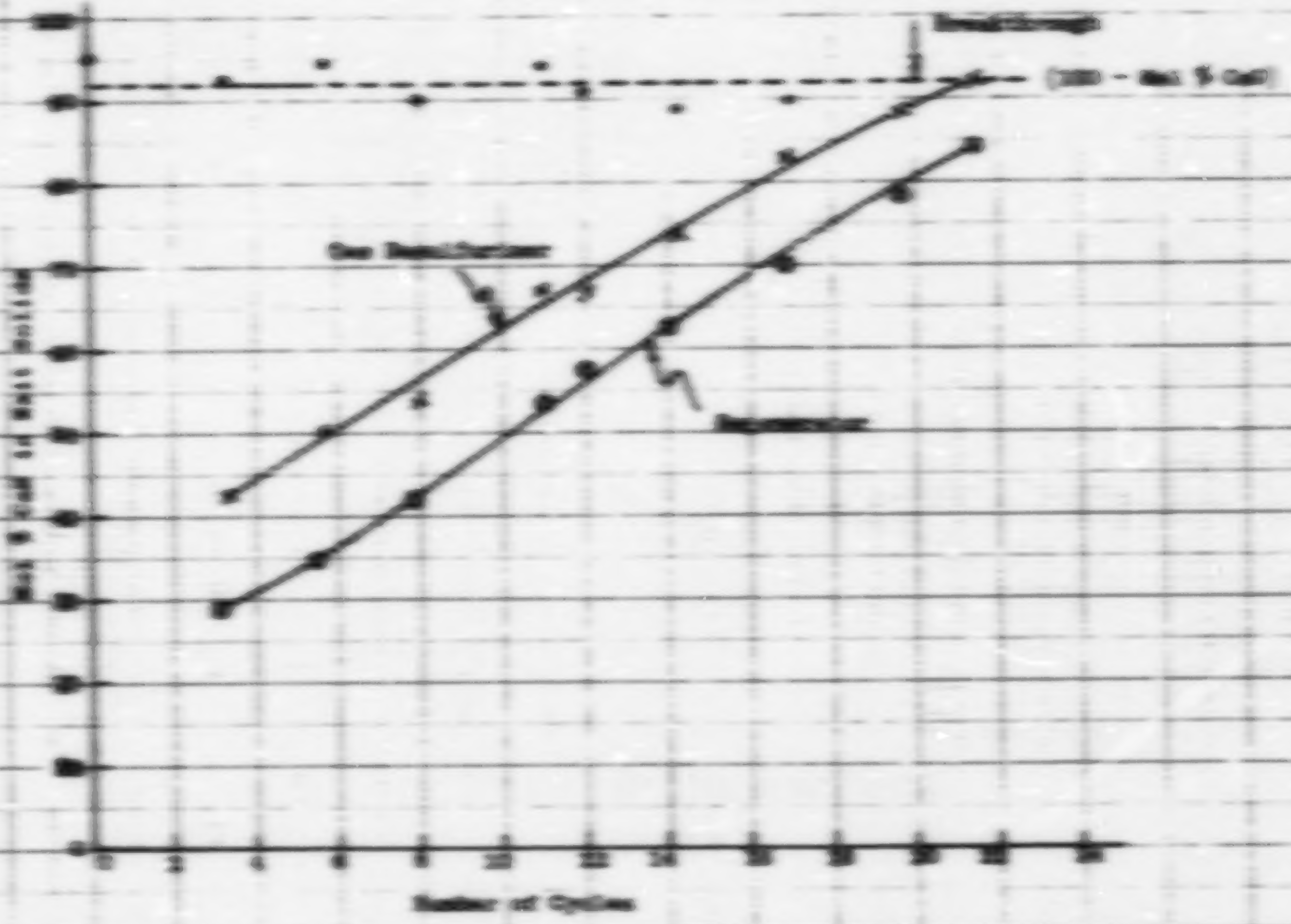
FIGURE IX-6

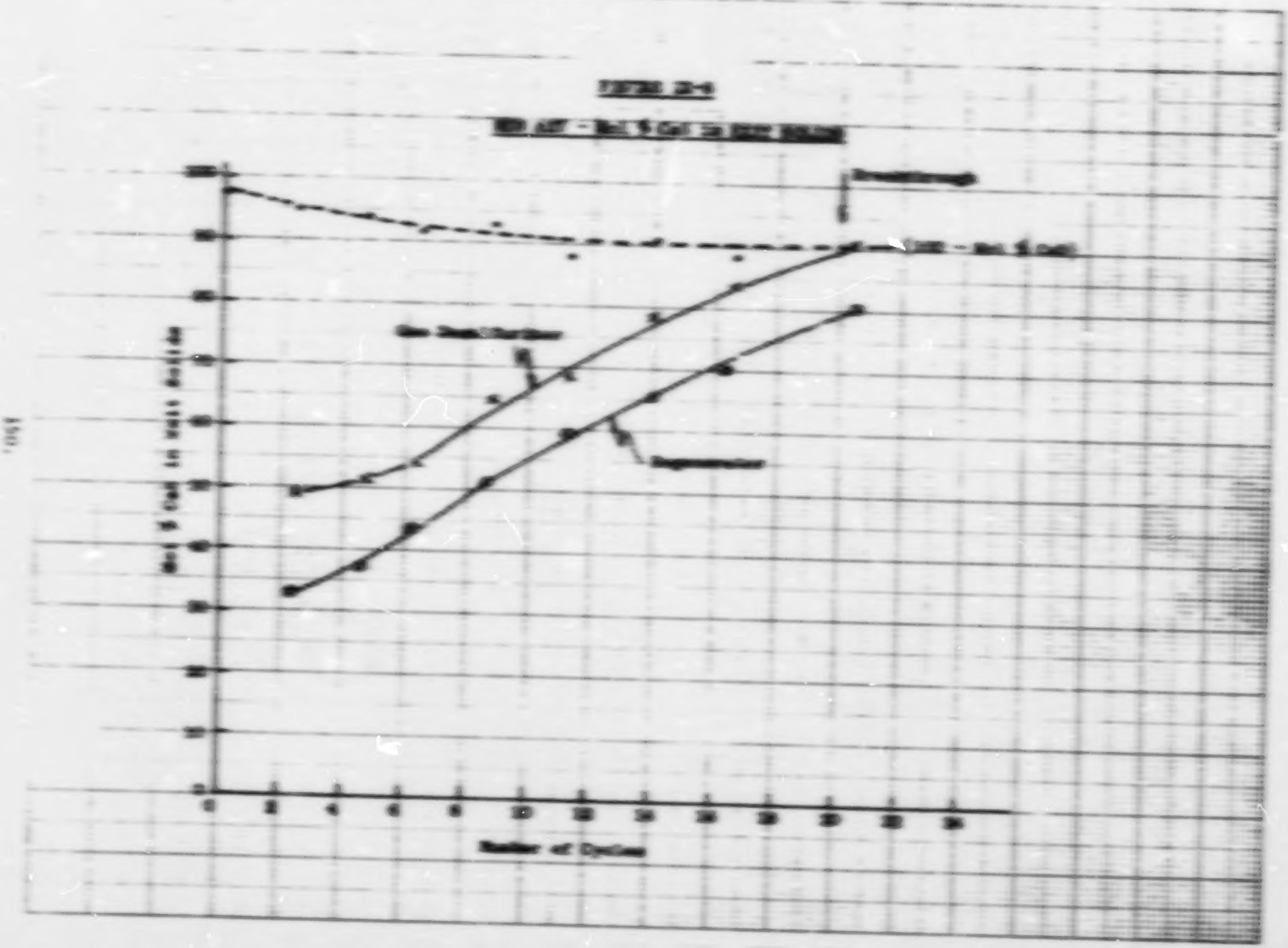
Deactivation of Hardened Tymochtee 10 Dolomite
at 704°C (1300°F)



[illegible]

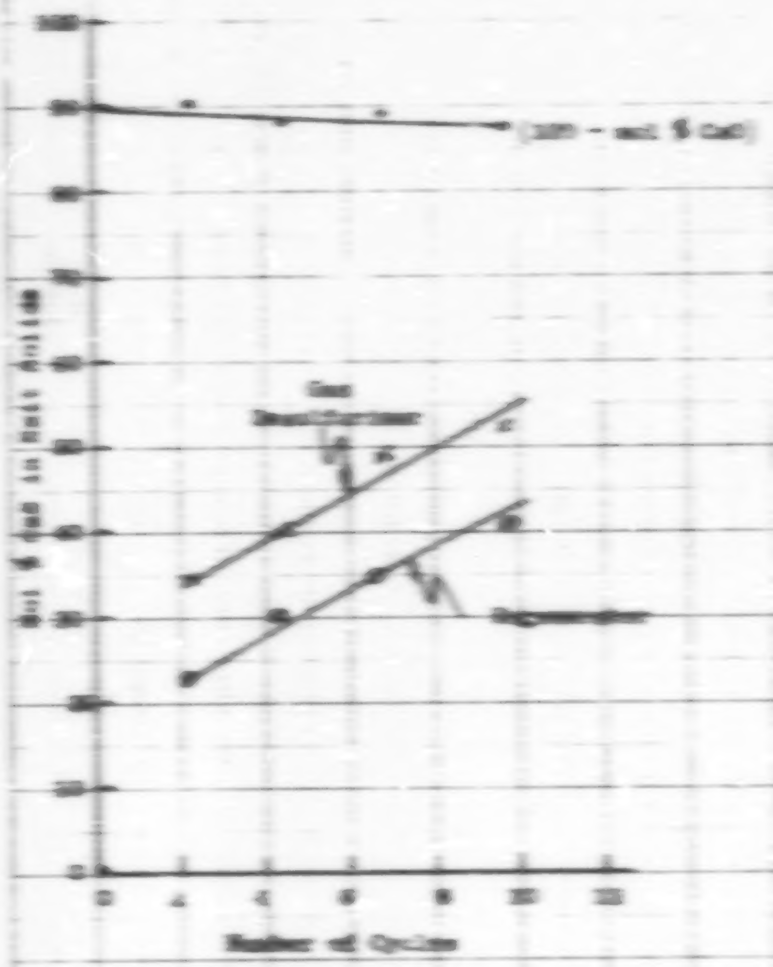
[illegible]


Breakthrough
Number of Cycles
0
2
4
6
8
10
12
14


Breakthrough
Number of Cycles
0
2
4
6
8
10
12
14
16
18
20
22
24
0
10
20
30
40
50
60
70
80
90
100

[illegible]

[illegible]


100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
Number of Cycles
Gas Desulfurizer
Regenerator

[illegible]

[illegible]

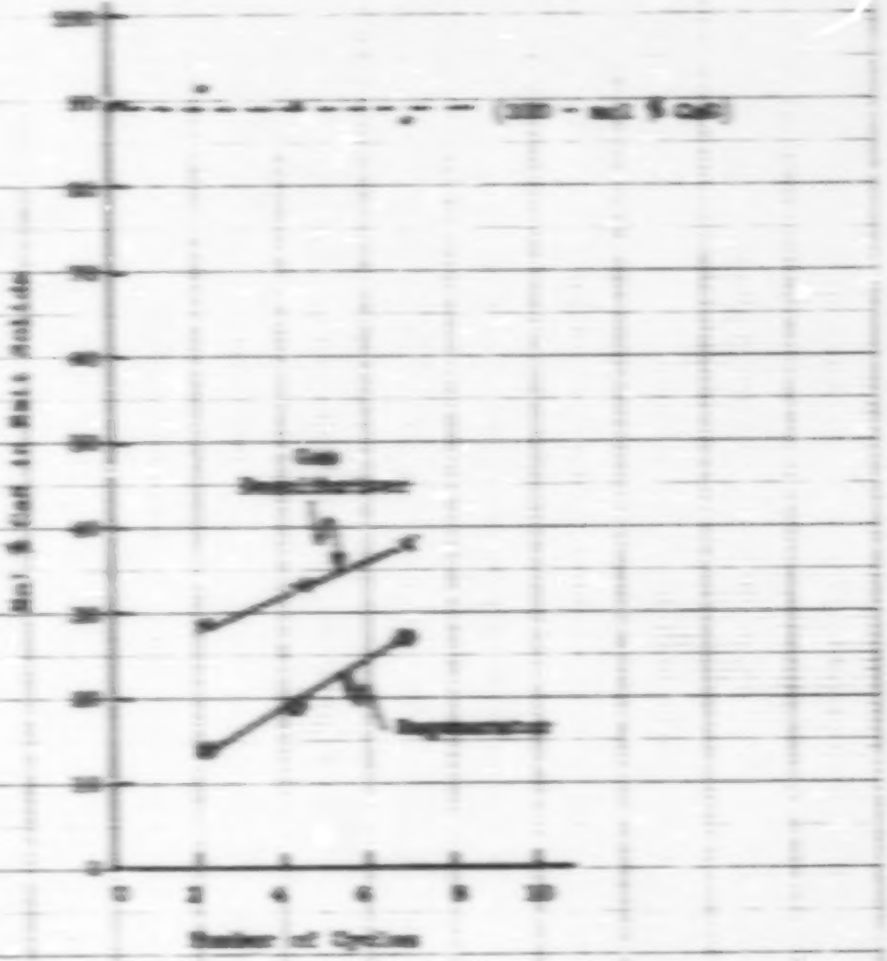
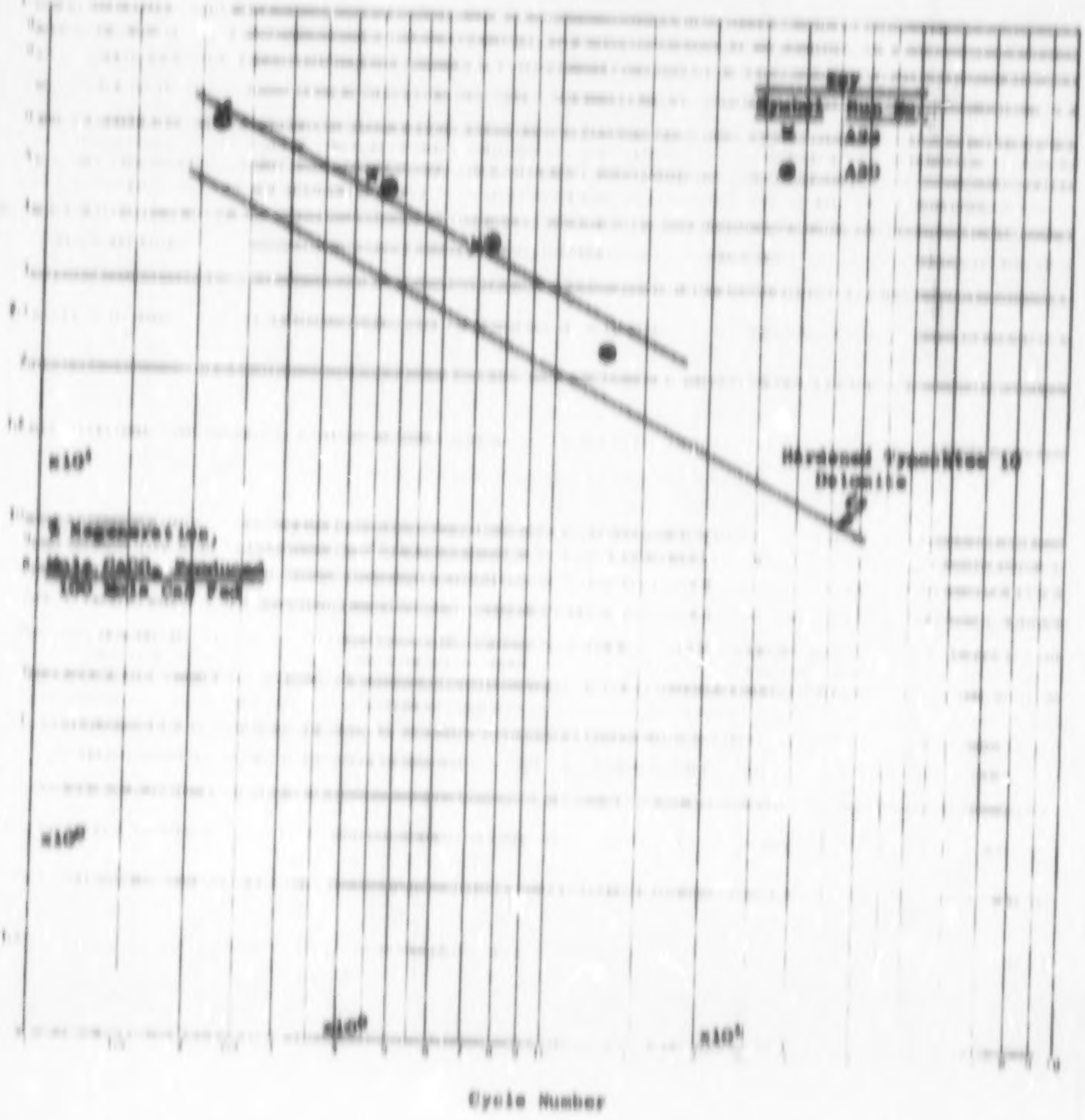

0
2
4
6
8
10
Number of Cycles
Gas Desulfurizer
Regenerator

FIGURE IX-11

Deactivation of Tymochtee 10 Dolomite at 704°C (1300°F)



Run A30

Run A30 was a blank hardening run, i.e., all the process steps of "sulfidation" and oxidation of Tymochtee dolomite were carried out but no H_2S was fed to the hardening process. The purpose of the run was to check the possibility that hardening involved reaction of impurities in the stone with CaS or other forms of Ca. The original hypothesis was that a low melting $CaCO_3$-$CaSO_4$ transient liquid was involved.

The initial attrition rate was 3.9% but this fell to 1.0% by cycle 13. By comparison, Tymochtee dolomite which had been hardened via a 30% sulfiding-oxidation procedure showed an attrition rate of 0.7% from the first cycle. It is concluded that, to be immediately effective as a hardening step, oxidation must be carried out on a sulfided stone. Oxidation per se is beneficial in that hardening apparently takes place as the acceptor is cycled and the CaS concentration increases. However, such secondary hardening is slow. The data indicate that hardening involves reaction of CaS or other forms of Ca with oxidized impurities in the acceptor. With a very impure stone, such a phenomenon could possibly lead to agglomerate formation as is suspected to have occurred with limestone 1691 during Run A13.(1)

As in Run A29, the regeneration activity was superior to that of the hardened Tymochtee 10 stone. It would appear that hardening does cause a loss of activity even at the relatively mild conditions employed in Runs A26 to A29. The run data are shown in Figure IX-10, and the regeneration data are given in Figure IX-11.

Run A30A

Run A30A was made to check the attrition rate of untreated Tymochtee dolomite. The run was initiated by substituting sufficient untreated stone into the feed hoppers to displace the A30 inventory. The unit was not shutdown, and conditions for A30A were the same as for A30. An attrition rate of 2.0% of the feed rate was observed, and Run A30A was continued only long enough to check the attrition rate.

The attrition rate of 2.0% was lower than had been expected since previous runs under similar conditions had shown attrition rates 3.5, 5.6 and 4.9%. The fact that the current work was done with a different shipment of stone, albeit from the same quarry, may have been the reason for the difference.

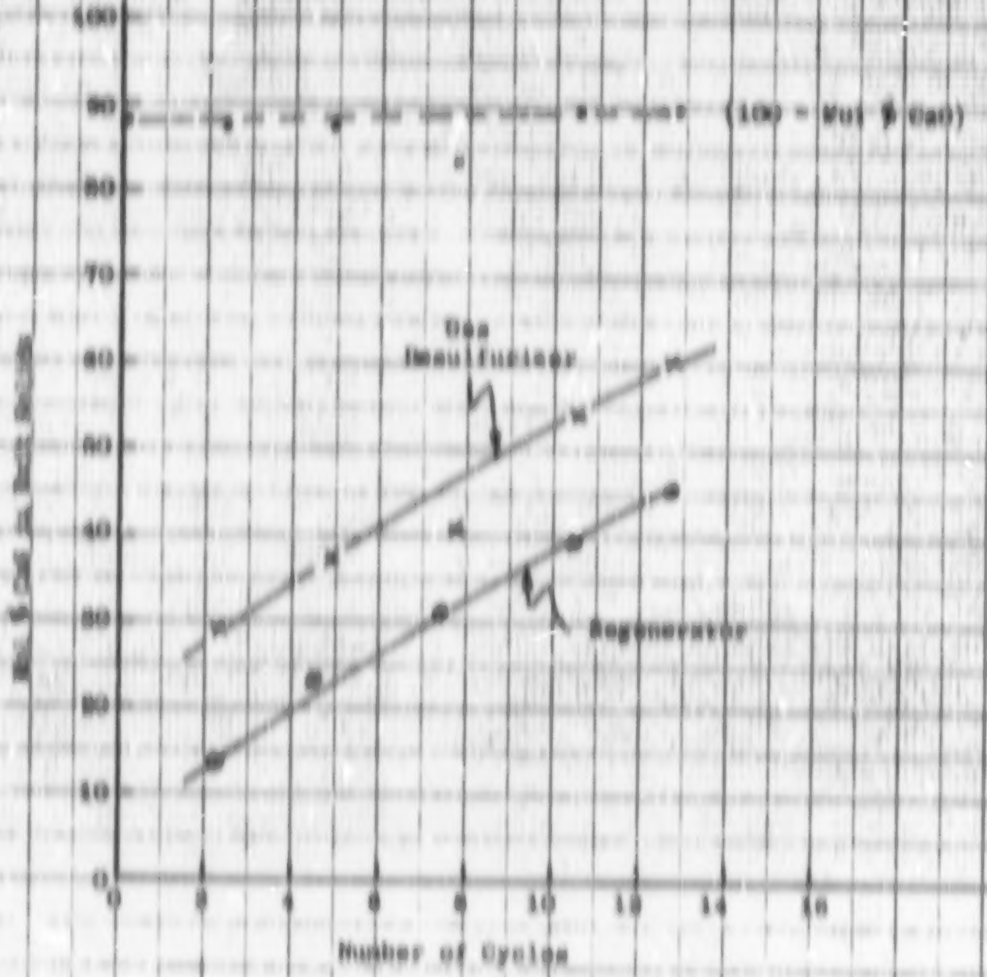
CaO Formation

The data for Run A30 in Table IX-3 show a 12% loss of $CaCO_3$ just on calcination at process conditions. It must be concluded that, at run conditions, reaction occurs between $CaCO_3$ and impurities in the stone which uses up ca. 10% of the calcium. "CaO" formation thus is actually loss of $CaCO_3$ by reaction with impurities. For this to be true, the reaction must take place to an extent beyond that seen in the assay of the fresh stone. In the fresh stone assay, the solid is exposed to 1 atm CO_2 for 15 minutes at 1550°F (844°C). As the run temperature is only 1600°F (871°C), the additional loss observed in the continuous unit was not anticipated.

It is noted that in the previous work with Tymochtee dolomite, which was performed under Contract EHSD-71-15,(1) the CaS content of sulfided stone was determined by difference based on the measured $CaCO_3$ content. If loss of

FIGURE IX-12

Run A20 : Mol % CaS in Melt Solids



$CaCO_3$ to a nonsulfided form occurred at run conditions, the calculated initial sulfide content would be high by ca. 15 mol %. Review of the data show this to be the case. The high calculated sulfide levels had originally been ascribed to irregularities in the startup of the liquid H_2S feed system.

The use of separate analyses for $CaCO_3$ and CaS was begun late in the previous contract period (EHSD-71-15). At that time, Canaan dolomite, a pure stone, was being fed, and negligible discrepancies appeared when the $CaCO_3$ and CaS contents were summed.

As it was not practical to run a pressurized high-temperature assay in the lab, the present assay was retained. For consistency, data on calcium species is reported as it was since the beginning of this program with the understanding that "CaO" formation was really loss of $CaCO_3$ by reaction with impurities.

Clarification of the mechanism involved in $CaCO_3$ loss and in hardening would be aided by an intense physical and chemical examination of solids. Extensive work of this nature is not planned. However, the samples are being saved, and selected materials can be given over to in-depth study later.

D. Tymochtee No. 9 Dolomite

Various batches of Tymochtee dolomite had given uniform results in the CO_2 Acceptor Process.(1) The Tymochtee stone used for the work done under Contract EHSD 71-15(2) was the ninth batch received from the C. E. Duff quarry and was labeled Tymochtee 9. This was the feed for Runs A1, A3, A4, A18, A32, A36 and A37. Tymochtee 10 was received early in the reported contract period and was the feed for Runs A23-A30. The supply of Tymochtee 10 ran out, and Tymochtee 9 stone was used as the feed in a series of runs designed to evaluate the effect of particle size.

Run A38

The feed to Run A38 was 20 x 28 Tyler mesh Tymochtee 9 dolomite which had been hardened via sulfidation and oxidation as detailed in Tables IX-7 and IX-8. Upon cycling, two unexpected results were observed: regeneration activity was lower and the attrition rate was higher, i.e., 1.7% versus 0.7% attrition observed earlier with 28 x 48 mesh stones. Activity of the acceptor in the gas desulfurizer was normal. The run data are given in Figure IX-13, and the regeneration activity data are presented in Figure IX-14. The percent regeneration was 14% in cycle 5 and 11% in cycle 10. The activity of 28 x 48 mesh hardened Tymochtee 10 dolomite was 30% in cycle 5 and 31% in cycle 10. The run was shut down upon H_2S breakthrough in the gas desulfurizer during cycle 11.

The attrition rate was constant during the run at 1.7%. Analysis of collected overhead fines (Table IX-9) shows that 20-40% was +100 mesh where previously only about 10% +100 mesh stone appeared in the collected fines. Even after factoring out the contribution of coarser overhead stone, the attrition rate exceeded 1%. Presumably the +100 mesh overheads had been elutriated due to the high fluidizing velocity and the lack of freeboard for proper disengagement.

Run A39

The changes in attrition rate and activity which occurred in going from 28 x 48 mesh to 20 x 28 mesh hardened Tymochtee dolomite seemed anomalously

FIGURE 2-17

[illegible]

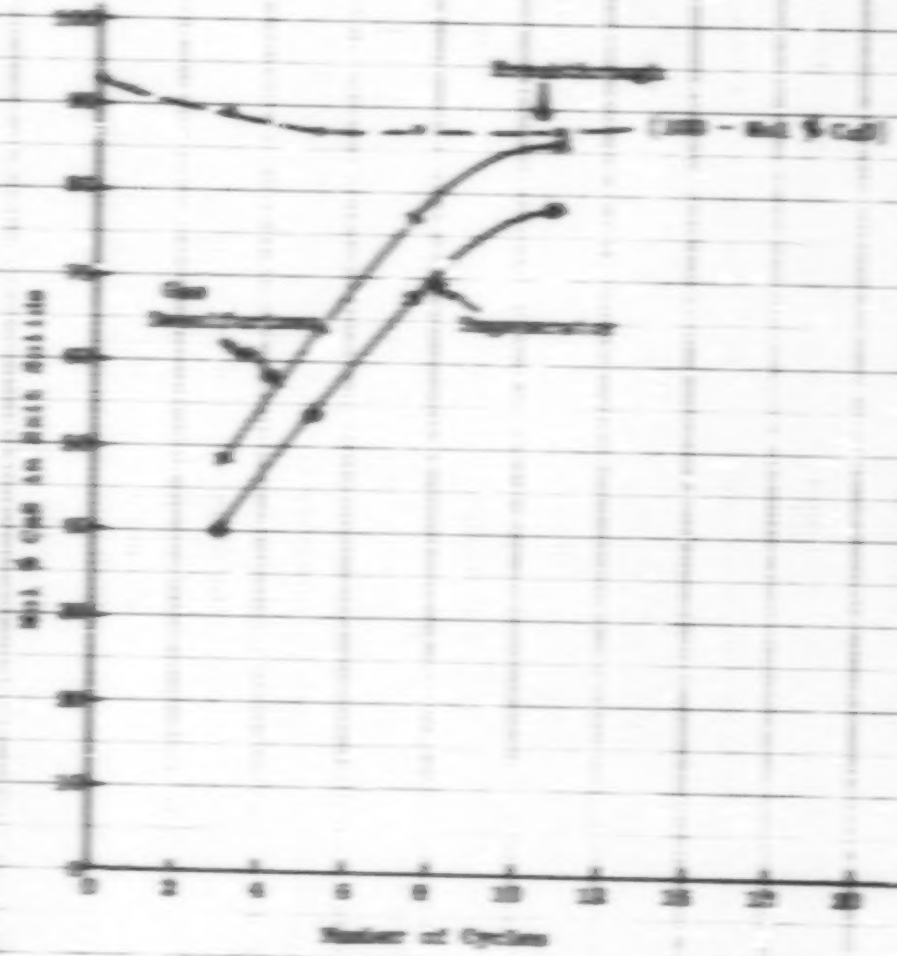
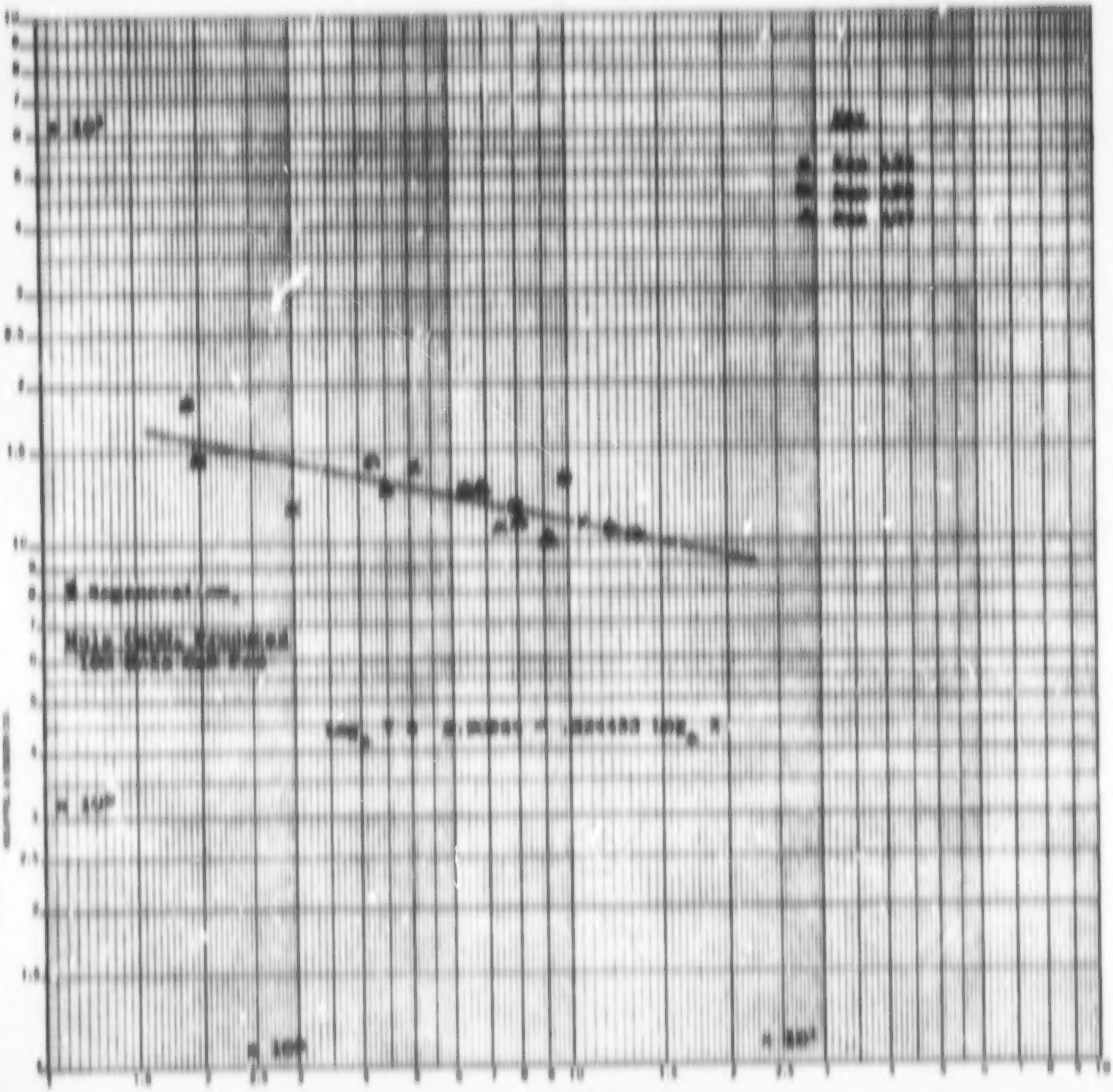


FIGURE IX-14

DEACTIVATION OF CaS IN HARDENED TYMOCHTEE D DOLOMITE AT 704°C (1300°F)



large. A hardened 28 x 35 mesh stone was run in A35 to better define the effect. The flow rate of lift gas was kept the same as for the 20 x 28 mesh case.

The attrition rate for the 28 x 35 mesh hardened Tymochtee 9 dolomite was 0.8%, the same as for the 35 x 48 mesh size Tymochtee 10. This result eliminated the possibility that higher lift gas rate per se was the cause of increased attrition of the 20 x 28 mesh size.

As given in Figure IX-14, regeneration activity was still significantly less than for 35 x 48 mesh Tymochtee 10 stone. Run data are given in Figure IX-15.

Run A37

Run A37 was made in order to obtain more data on the behavior of hardened Tymochtee 9 dolomite. It was thought that low activity obtained with 28 x 35 and 20 x 28 mesh stone in Runs A35 and A32, respectively, could be due either to a size effect interacting with the hardening procedure or to intrinsic differences in the stone.

Run A37 was made with hardened 35 x 48 mesh Tymochtee 9 dolomite. As shown in Figure IX-14, the regeneration activity was again low. The regeneration data is about the same for all three sizes tested, 20 x 28, 28 x 35 and 35 x 48 Tymochtee 9 stone. Run data are given in Figure IX-16.

E. Tymochtee No. 11 Dolomite

Several runs were also made with Tymochtee 11 dolomite. The regeneration activity of this stone was very similar to that of the Tymochtee 9 stone as can be seen from Figure IX-17. Run data are presented in Figures IX-18 to IX-21.

Run A38

Run A38 was made with Tymochtee 11 dolomite using 20 x 28 mesh as the size consist. The regeneration activity was about the same as that of Tymochtee 9. Due to an operating error, sulfidat in the hardening step was about 40% instead of the desired 80%.

Run A42

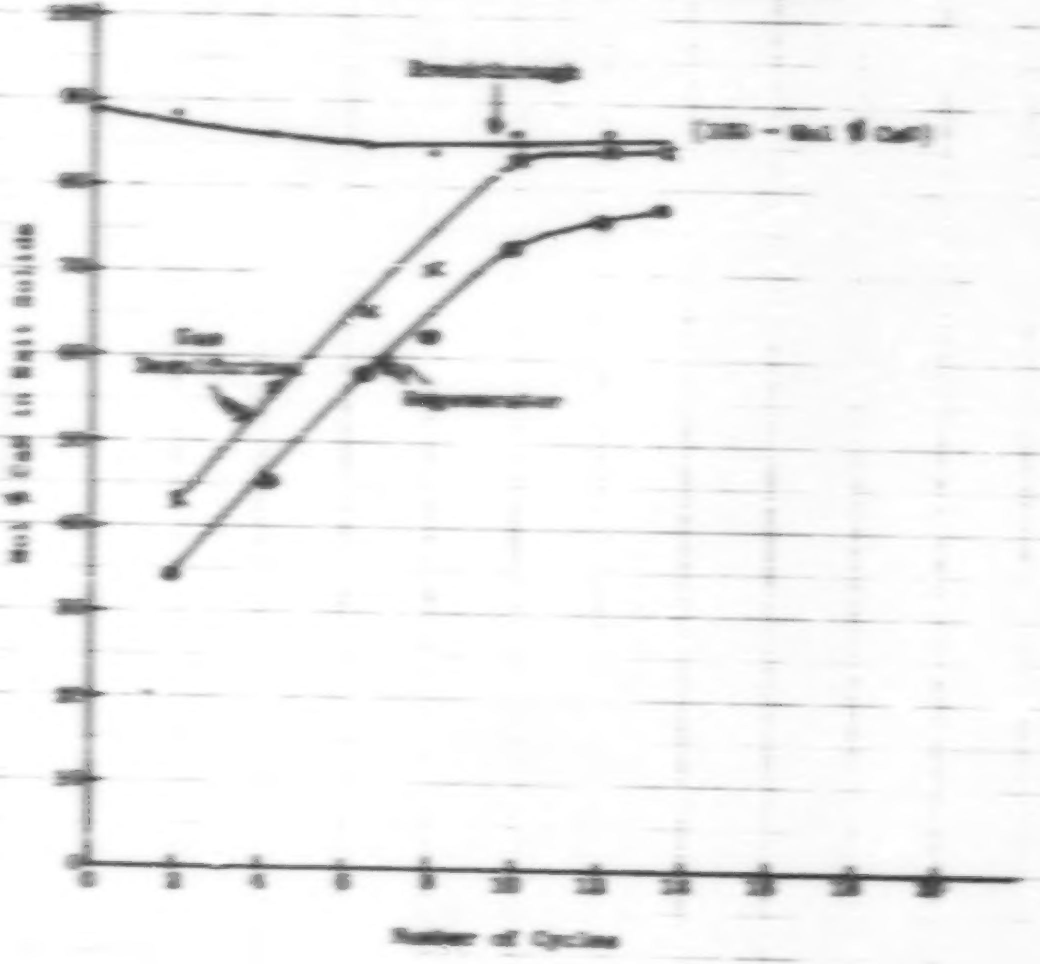
This run was made with 35 x 48 mesh Tymochtee 11 stone. As shown in Figure IX-17, there was no effect of changing the size consist upon regeneration activity. This confirmed the conclusion drawn from the Tymochtee 9 data that there is no effect of particle size upon regeneration activity in going from 20 x 28 to 35 x 48 Tyler mesh stone.

Run A45

Examination of sectioned sulfided stone had shown that, initially, the sulfur is predominantly distributed around the outside of the particle in a shell. The hardening procedure could conceivably close off the interior of the particle and thereby reduce the stone's activity. For Run A45, the sulfidation step in the hardening was conducted at 816°C (1500°F) instead of the usual 871°C. The lower temperature would increase the rate of H_2S diffusion into the particle in relation to the rate of reaction. Upon cycling, there was no significant change in activity, and the attrition rate of 1.4% was slightly higher than usual.

[illegible]

[illegible]


Breakthrough
(100 − Mol % CaO)
Gas Breakthrough
Regenerator
Mol % CaO in Melt Outside
Number of Cycles
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20

[illegible]

[illegible]

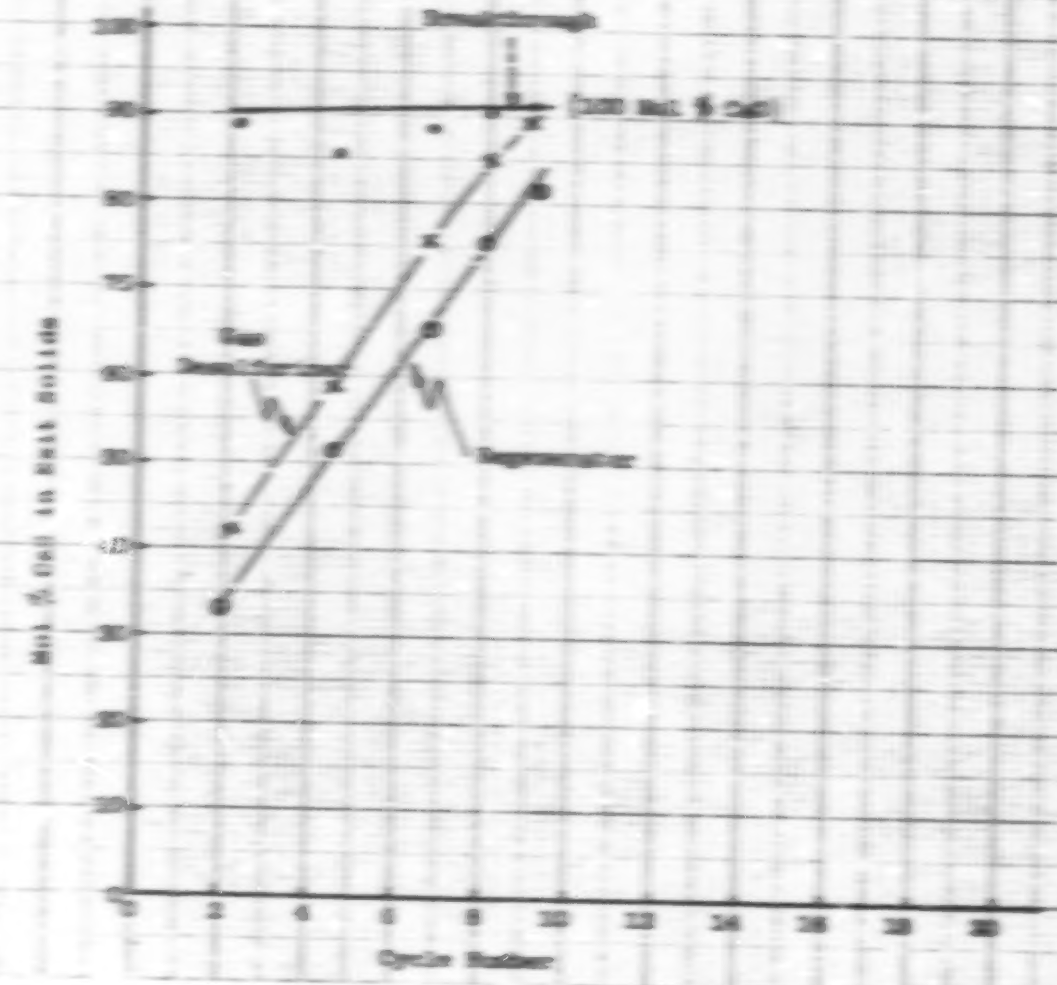
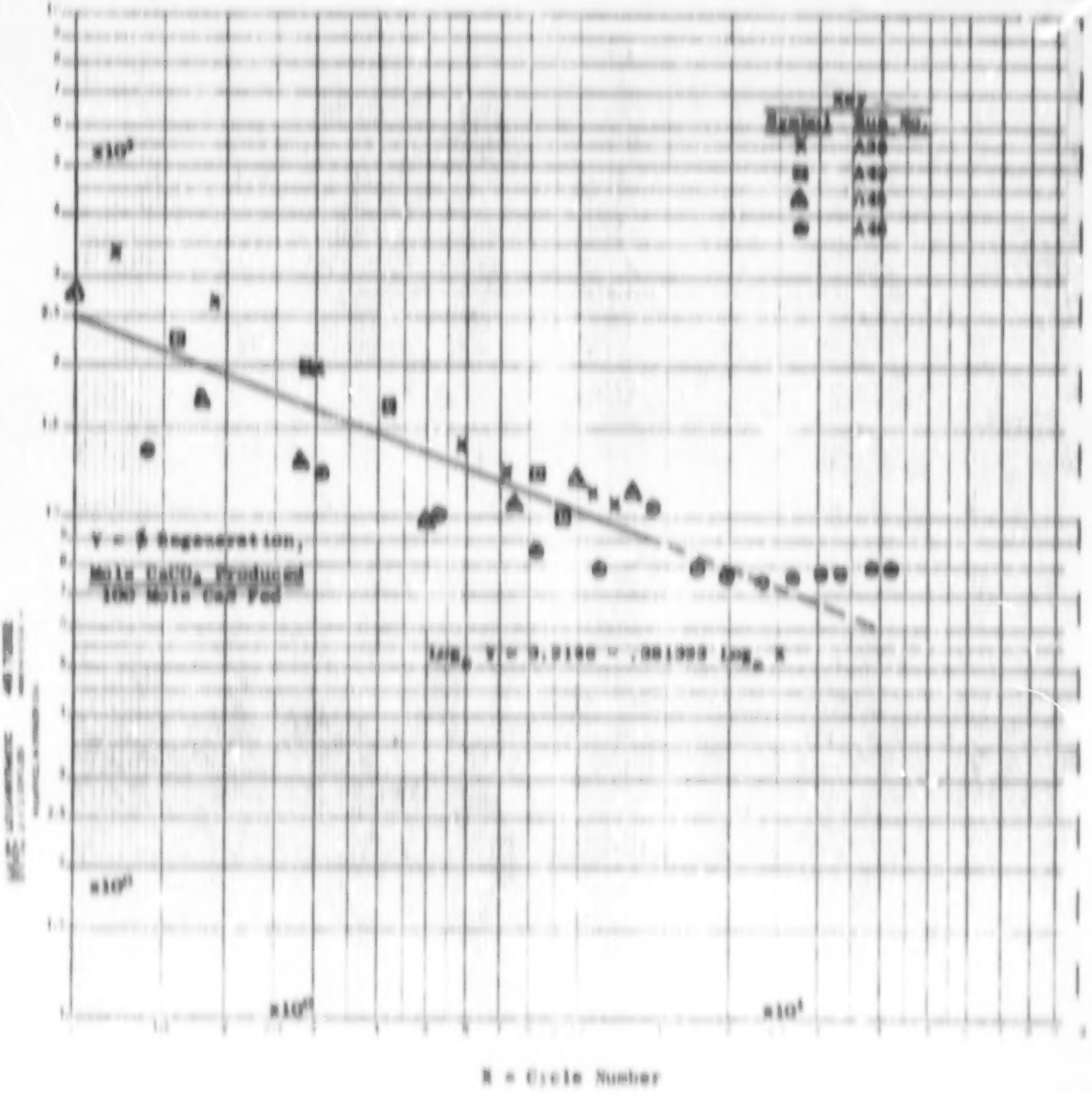

Breakthrough
Regenerator
Mol % [illegible] in Bulk Solids
Cycle Number
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
14
16
18
20
22

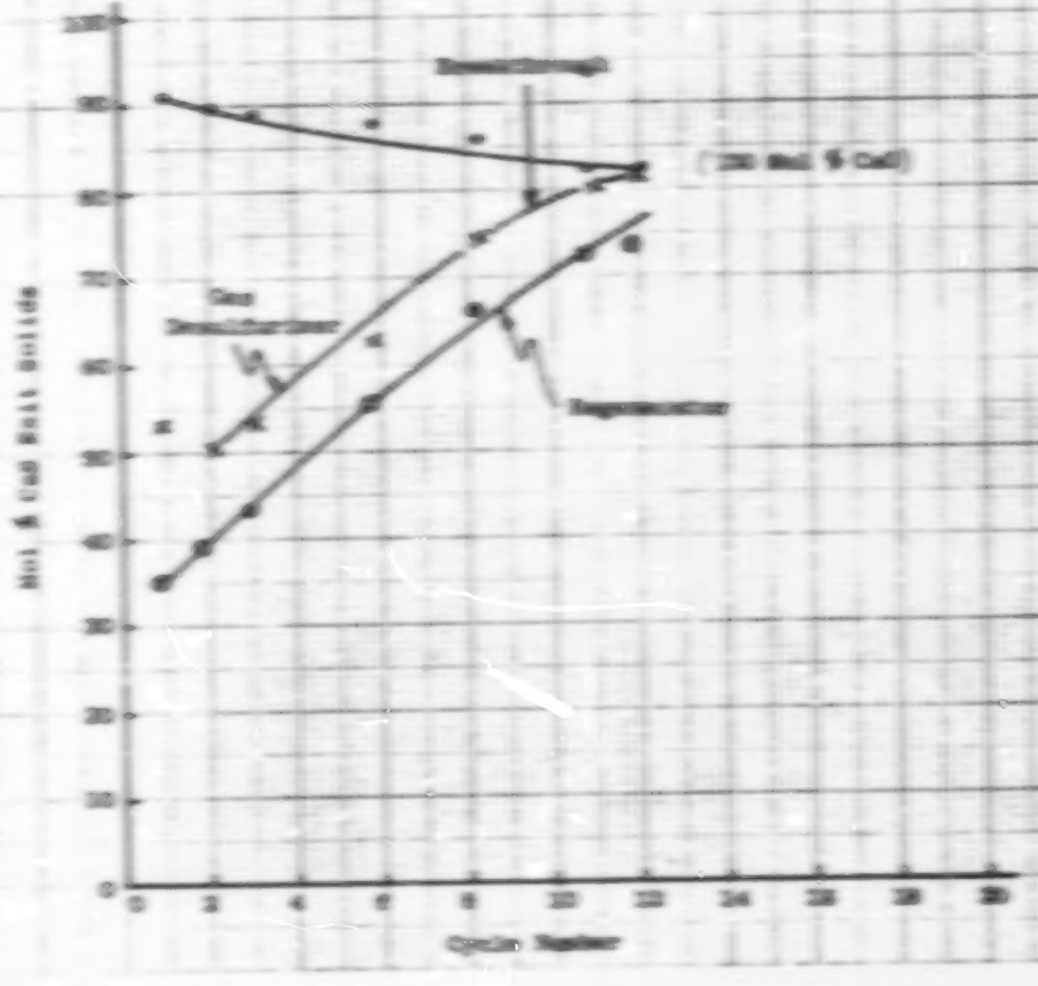
FIGURE IX-17

Deactivation of Tymochtee II Dolomite at 704°C (1300°F)



[illegible]

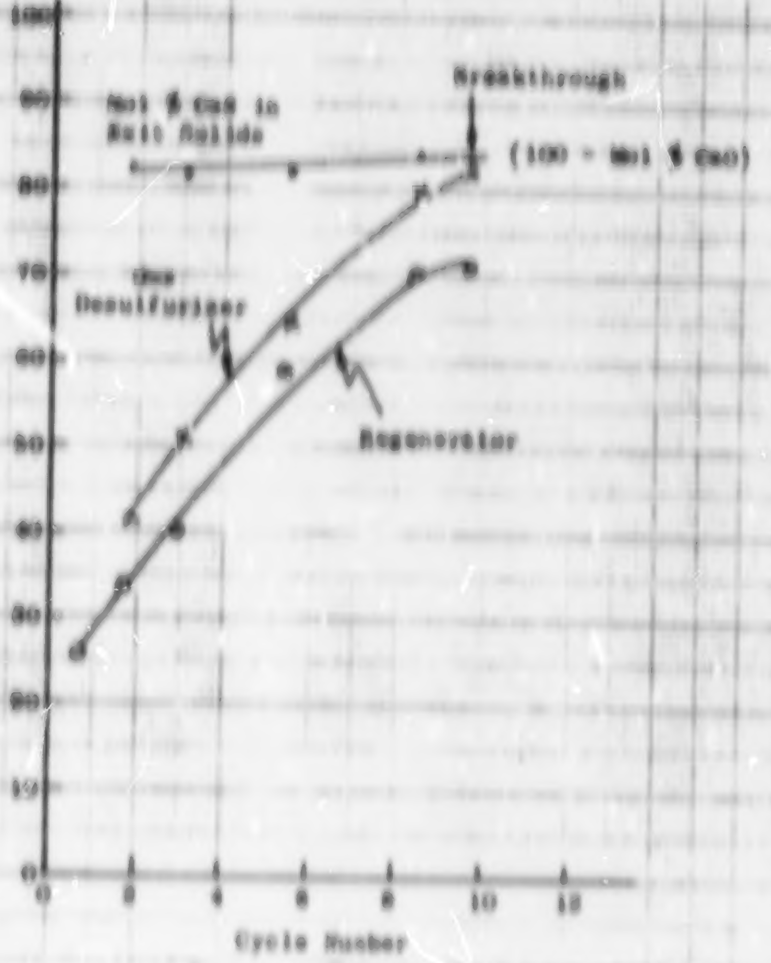
[illegible]



100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
18
20
Cycle Number
[illegible]
Gas Desulfurizer
Regenerator

FIGURE IX-10

RUN A48 - MOL % CaO IN EXIT SOLIDS



Run A46

This run was a demonstration of the behavior of hardened Tymochtee II dolomite for 42 cycles. A larger initial stone inventory was prepared so that depletion due to attrition would not force the run to end. An initial sulfidation conversion per pass of 12% helped to defer breakthrough until cycle 14. At that time the H_2S feed rate was cut to ca. 6% and no breakthrough occurred until the run was voluntarily terminated.

The purpose of this run was to get the experimental data on a large number of cycles, so the process design will rely less on extrapolation. However, the correlation in Figure IX-17 uses data from Run A46 only through 14 cycles.

When the H_2S feed was reduced, a drop in percent regeneration was observed in Run A46. The explanation for this follows. Consider a situation in which the stone has a 10% regeneration capacity and is being sulfided by 10% per cycle, e.g., entering the gas desulfurizer the $CaS:CaCO_3$ ratio is 90:10. Leaving the gas desulfurizer and regenerator the ratios are 100:0 and 90:10, respectively. If the H_2S input is reduced to 5% conversion, the ratio leaving the gas desulfurizer will be 95:5. Two possibilities exist for the regenerator. The CaS level may be reduced by 10% relative to 85.5% or, once having been formed, the CaS is resistant to regeneration and the CaS content cannot be reduced much below 90%. In the latter case, the observed percent regeneration would be 5%. Our experience has been that the second case is what actually occurs. In Run A46, after the H_2S input was reduced, the regeneration fell and remained nearly constant, and the CaS content of stone leaving the regenerator was not significantly lowered.

F. Buchanan Dolomite

Four runs were made in which hardened Buchanan dolomite was the feedstock. The hardening conditions are detailed in Tables IX-10 and IX-11. These were essentially the same as had been run on the Tymochtee stone. Detailed conditions for the gas desulfurizer and regenerator are given in Tables IX-12 and IX-13, respectively. Graphical data are presented in Figures IX-23 to IX-26.

Run A33

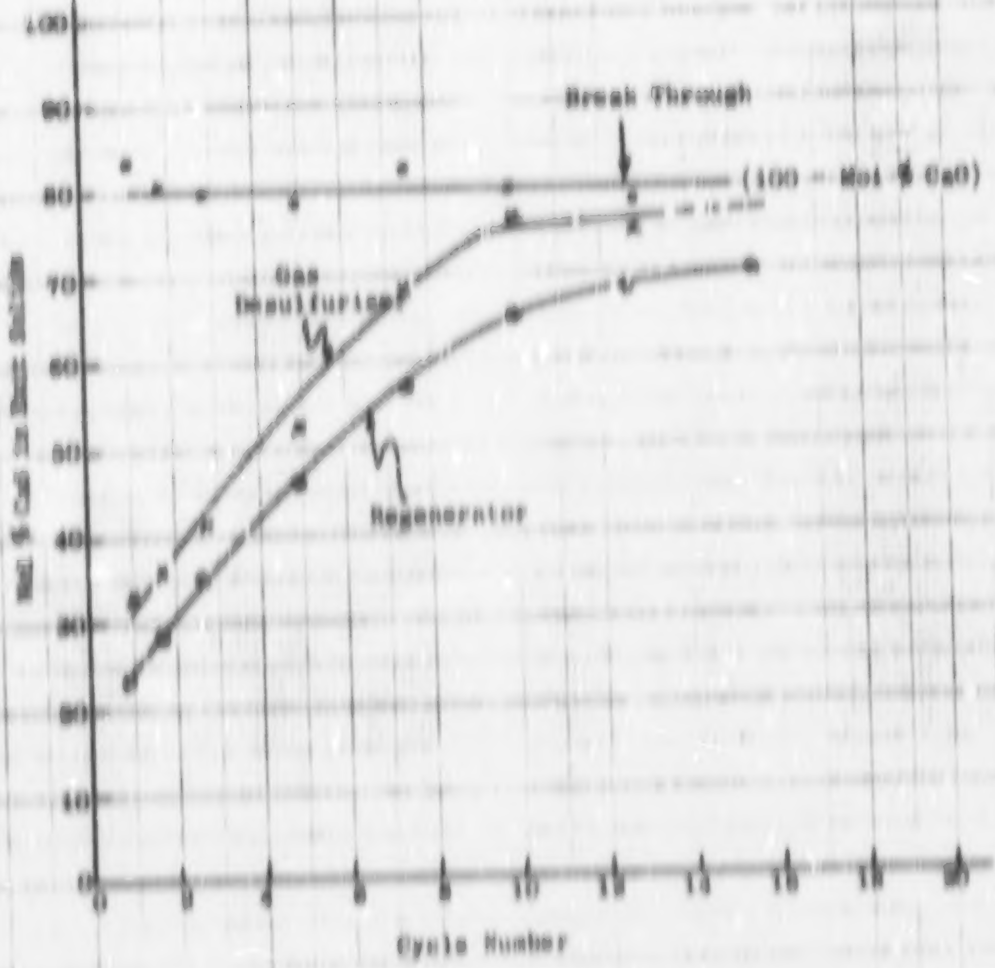
The feed to Run A33 was 20 x 28 mesh Buchanan dolomite which had been hardened via sulfidation followed by oxidation of ca. 10% of the calcium. The regeneration activity was 80% in cycle 3 and 17% in cycle 10 (Figure IX-23). The attrition rate was initially 1.8% and rose to 6.4% in cycle 11. The latter figure is about the same as for Buchanan stone which had not been hardened. As in Run A28, some 35% of the overhead solids were +100 mesh. The high attrition rate caused the run to shut down due to depletion of the stone inventory.

Run A43

Run A43 was a repeat of A33, except for the use of 35 x 48 mesh feed. The regeneration behavior was essentially the same again confirming that there is no effect of particle size on this variable. The attrition rate was 8.1%.

FIGURE II-20

RUN A43 - MOL % CaS IN EXIT SOLIDS



[illegible]

[illegible]

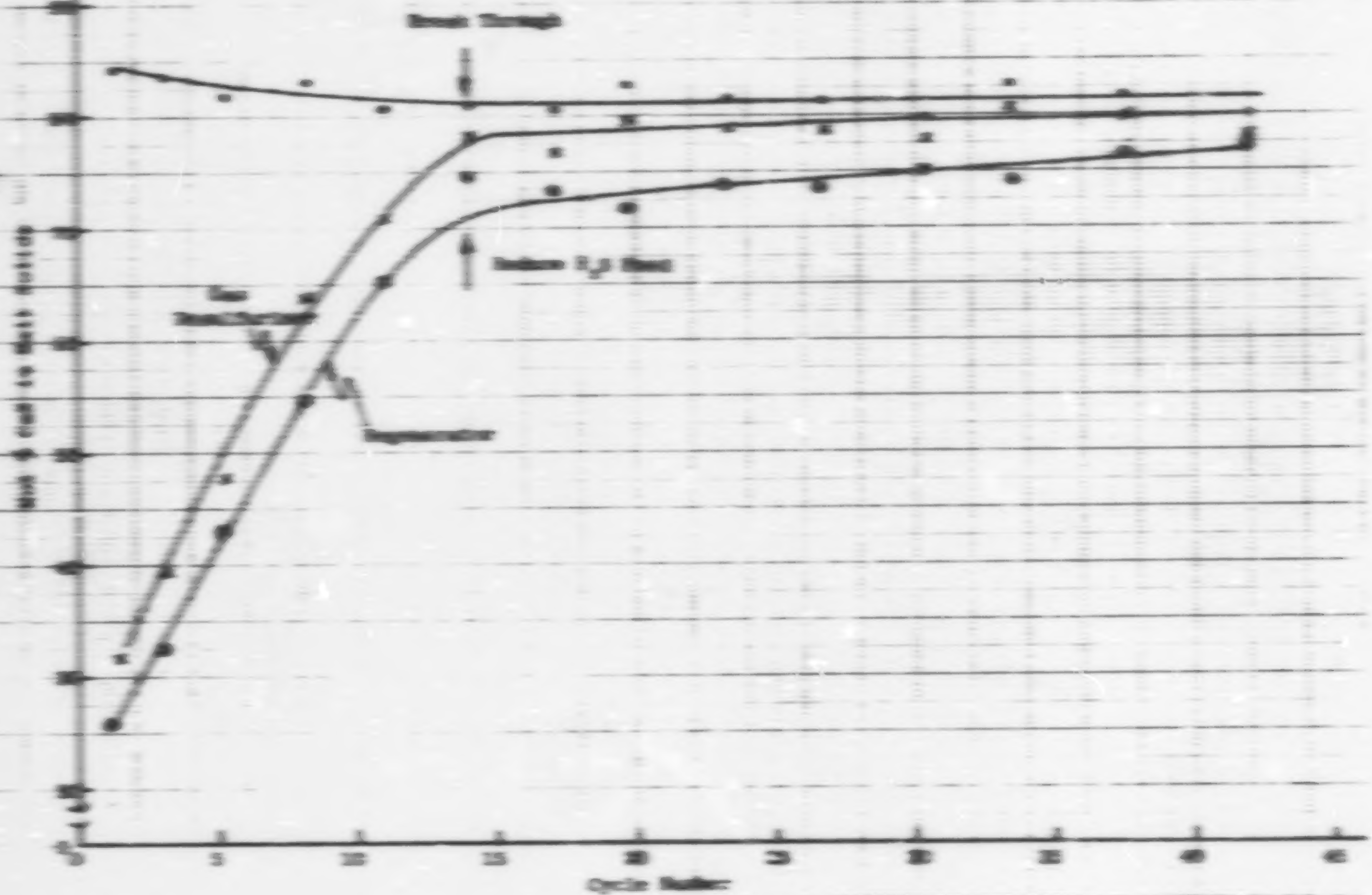

Break Through
[illegible]
0
5
10
15
20
25
30
35
40
45
Cycle Number

TABLE IX-10

Conditions for Continuous Sulfidation of Buchanan Dolomite

System Pressure: 15 atm (206 psig)
System Temperature: 871°C (1600°F)

Run Number	A33	A42	A44A	A47
Acceptor	Buchanan 2	Buchanan 3	Buchanan 3	Buchanan 3
Acceptor Size Consist, Tyler mesh	20 x 28	35 x 48	35 x 48	35 x 48
Feed Rate, gm/hr (raw basis)	1770	2090	1028	1129
Nominal Solids Residence Time, min	90	72	158	165
Input, SCFH				
Recycle to Bed	310	148	148	148
H_2O	60	21.4	21.4	21.4
H_2	55	25.0	25.0	25.0
CO	62	20.0	23.0	23.0
CO_2	31.0	6.8	6.8	6.8
N_2	152	66	66	66
H_2S	1.8	1.8	1.8	1.8
Purges (CO_2) to Bed	5	5	5	5
Purges (N_2) above Bed	15	15	15	15
Recycle Acceptor Lift Gas, above Bed	110	110	110	110
Mol % CaS in Product Solids	13	13	35	35

TABLE IX-11

Conditions for Continuous Oxidation of Sulfided Buchanan Dolomite

System Pressure: 15 atm (206 psig)
System Temperature: 871°C (1600°F)

Run Number	A33	A42	A44A	A47
Feed Rate, gm/hr (adjusted to maintain O_2 breakthrough)	1200	1125	841	810
Nominal Solids Residence Time, min	103	83	233	198
Input, SCFH				
Recycle to Bed	340	138	138	138
CO_2	140	40	40	45
N_2	165	90	90	90
Air	18	18	18	18
Purges (CO_2) to Bed	5	5	5	5
Purges (N_2) above Bed	15	15	15	15
Recycle Acceptor Lift Gas	110	110	110	110

TABLE IX-12

Conditions and Results for Gas Desulfurizer with Buchanan Dolomite

System Pressure: 15 atm (206 psig)
System Temperature: 871°C (1600°F)

Run Number	A33	A43	A44A	A47
Type of Dolomite	Buchanan 2	Buchanan 3	Buchanan 3	Buchanan 3
Feed Reference	A33	A43	A44A	A47
Acceptor Size Consist, Tyler Mesh	20 x 28	35 x 48	35 x 48	35 x 48
Nominal Feed Rate, gm/hr (half-calcined basis)	1870	2100	2030	1940
Nominal Solids Residence Time, min	50	42	44	46
Input, SCFH				
Recycle to Bed	310	148	148	142
H_2O	60	21.4	21	21
H_2	55	25	26	27
CO	62	23	23	22
CO_2	21	6.8	9	9.5
N_2	152	66	66	66
H_2S	1.8	1.8	1.8	0.84(c)
Purges (CO_2) to Bed	5	5	5	5
Purges (N_2) above Bed	15	15	15	15
Recycle Acceptor Lift Gas, above Bed	110	110	110	110
Output in Cycle	11	18	7	21
Exit Gas Rate, SCFH (dry basis)	318	143	147	144
Composition, Mol %				
H_2	19.4	18.4	18.4	20.8
CO	18.5	17.2	17.2	16.7
CO_2	6.8	9.8	7.4	7.4
N_2	57.8	58.5	56.9	55.1
H_2S	0.03	0.12(a)	0.02	0.01
Outlet Gas, Top of Bed				
Composition, Mol %				
H_2O	8.0	8.1	8.0	8.1
H_2	18.1	15.9	17.9	20.2
CO	17.2	16.7	16.6	16.9
CO_2	6.0	9.8	7.2	7.1
N_2	47.6	49.7	50.5	48.4
H_2S	0.03	0.12	0.03	0.01
Flow Rate, SCFH, Top of Bed	672	301	304	301
Fluidizing Velocity, ft/sec	0.38	0.43	0.43	0.43
Attrition, % of Feed Rate	3.9(b)	2.1	0.8	0.88
Duration of Circulation with H_2S Feed, hr	37	53	43	235
Removal of Feed Plus Recycle Sulfur, %	90	83	98.3	98
% H_2S in Outlet/Equilibrium % H_2S	1.3	5.0	1.7	0.8
Conversion of Acceptor/Pass, mol %	15.5	13.1	14.6	8.4

(a) Gas sample taken after H_2S breakthrough.
(b) Includes 20-30% +100 mesh particles.
(c) For cycles 0 to 32.2 the H_2S feed rate was 1.8 SCFH.

TABLE IX-13

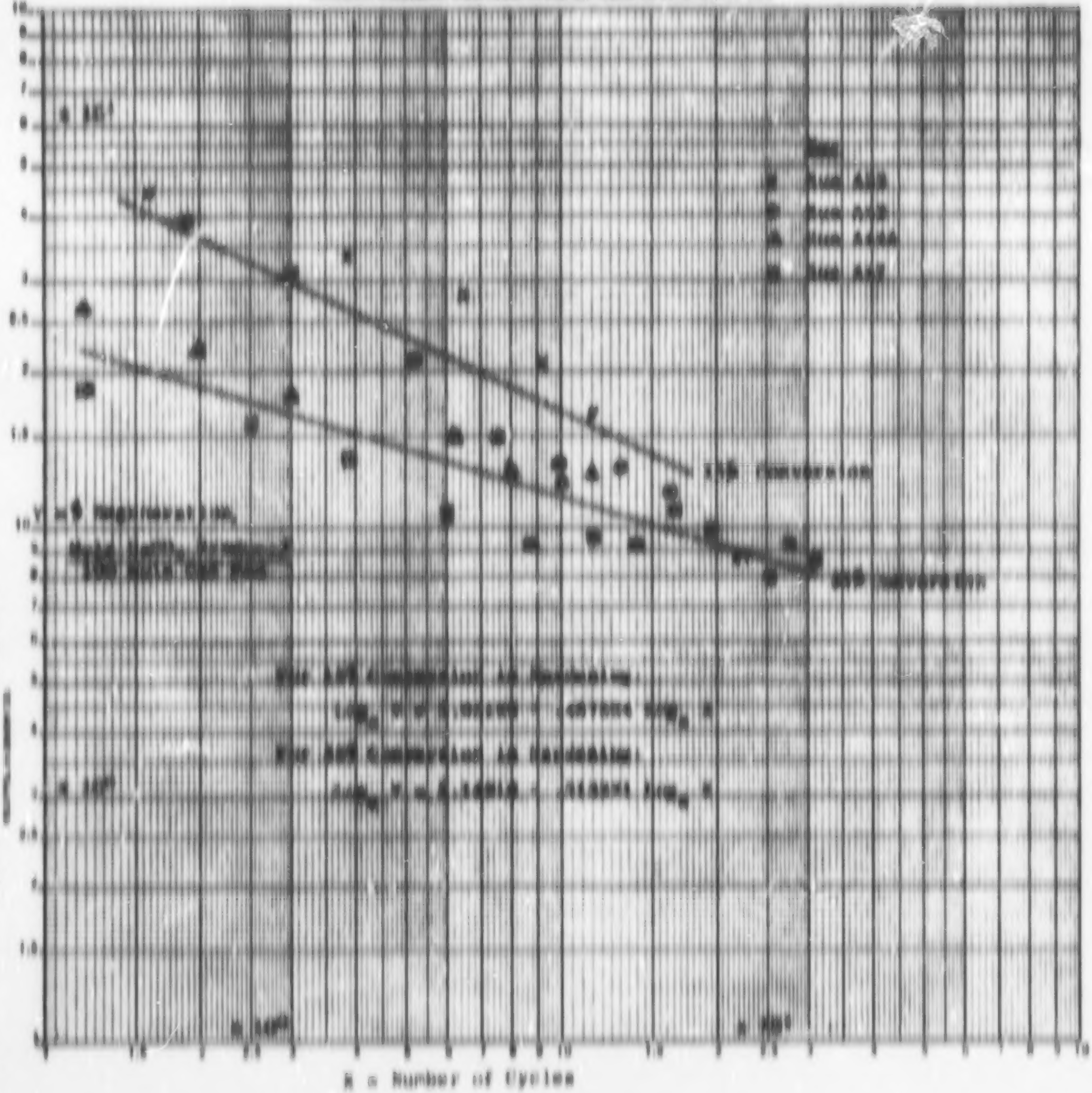
Conditions and Results for Regenerator with Buchanan Dolomite

System Pressure: 15 atm (206 psig)
System Temperature: 704°C (1300°F)

Run Number	A33	A43	A44A	A47
Nominal Solids Residence Time, min	58	51	53	55
Input, SCFH				
Recycle to Bed	0.0	35	35	38
H_2O	108	81	91	81
H_2	11	5.0	5	5
CO_2	205	70	70	70
Purges (CO_2) to Bed	10	10	10	10
Purges (CO_2) above Bed	15	15	15	15
Output in Cycle	11	16	7	21
Exit Gas Rate, SCFH (dry basis)	222	107	104	108
Composition, Mol %				
H_2	3.3	3.7	2.5	3.1
CO	1.6	1.9	2.1	1.8
CO_2	94.0	93.3	93.1	94.4
N_2	0.4	0.8	0.5	0.4
H_2S	0.58	1.70	1.66	0.56
COS	0.03	0.07	0.08	0.03
Outlet Gas, Top of Bed				
Composition, Mol %				
H_2O	34.5	38.5	38.3	30.7
H_2	2.2	2.3	2.0	2.4
CO	1.3	1.5	1.7	1.2
CO_2	61.3	56.1	56.3	65.0
N_2	0.3	0.4	0.6	0.3
H_2S	0.41	1.30	1.33	0.44
COS	0.02	0.05	0.05	0.02
Flow Rate, SCFH, Top of Bed	318	178	173	189
Fluidizing Velocity, ft/sec	0.87	0.48	0.48	0.50
% H_2S in Outlet/Equilibrium % H_2S	0.10	0.36	0.36	0.11
Regeneration of Acceptor/Pass, mol %	11.8	14.8	14.3	5.8

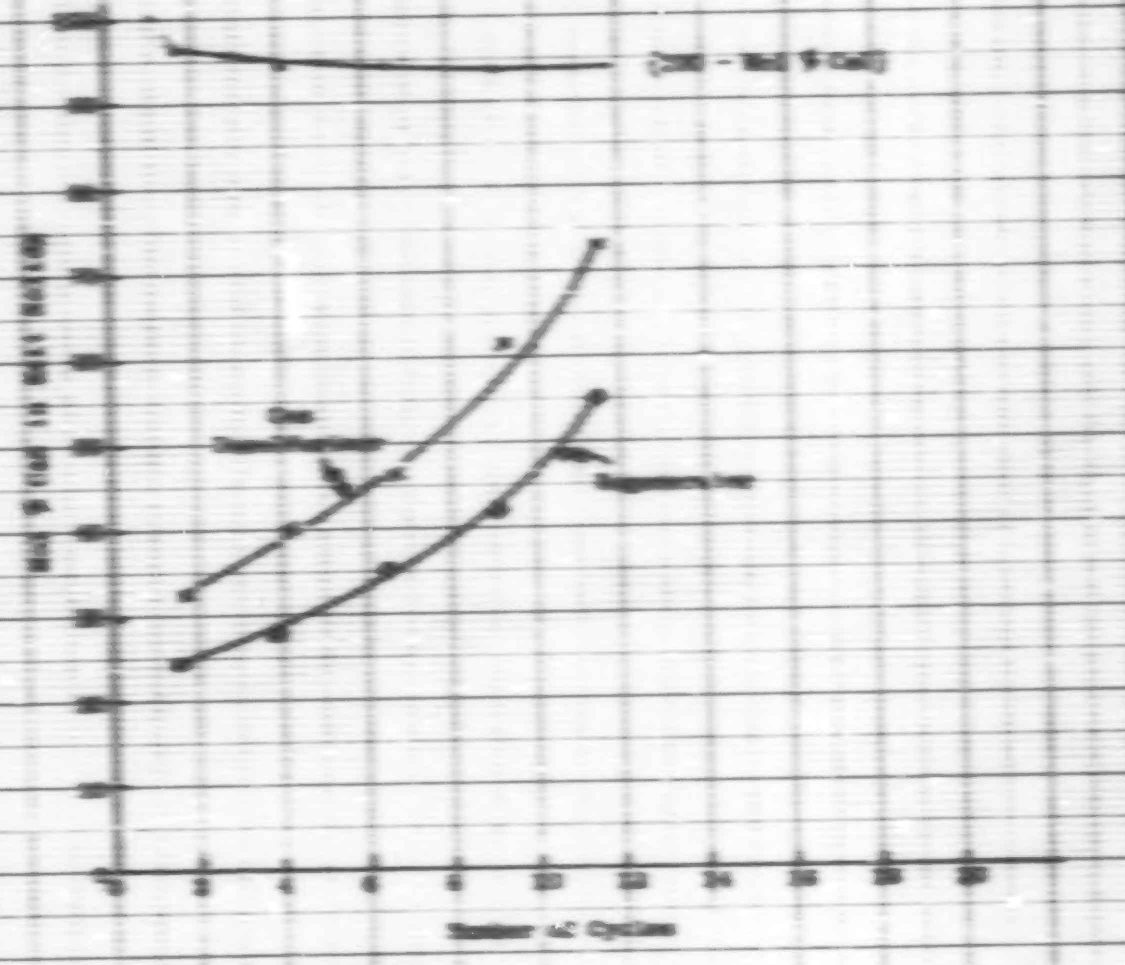
FIGURE IX-[illegible]

DEACTIVATION OF CaS IN HARDENED BUCHANAN DOLOMITE AT 704°C (1300°F)



[illegible]

[illegible]



0
2
4
6
8
10
12
14
16
18
20
Number of Cycles

Run A44A

The feed to A44A was hardened at 35% sulfidation rather than the 15% used earlier. The attrition rate was 0.8% and, as shown in Figure IX-26, the activity was lowered to about the same level as had been observed with Tymochtee 8 and 11 dolomites.

Run A47

Run A47 was a demonstration of the behavior of hardened Buchanan 3 dolomite for 55 cycles, the longest that any stone had been run. The sulfidation conversion was ca 10% until cycle 33 when breakthrough occurred. The H_2S feed was then reduced to give 5% conversion and no breakthrough occurred until the run was voluntarily terminated. Good $CaCO_3$ activity was observed for the entire run and regeneration proceeded normally. The overall attrition rate was 0.7%. The run confirmed that hardened Buchanan dolomite would be suitable for use in the process.

Figure IX-26 graphically presents the regeneration data for four runs with hardened Buchanan dolomite, two at 15% sulfidation in the hardening step and two at 35%. It appears that the activity of the stone is reduced due to the higher conversion in the hardening sequence. However, the higher conversion was accompanied by proportionately longer residence times in both the sulfiding and oxidation steps, and the reduction in activity may have been due to the extended hold at temperature rather than the specific conversion level. Specifically, in Runs A33 and A43 residence times average 85 and 95 minutes, respectively, in the sulfiding and oxidizing steps of the hardening procedure. The comparable numbers for Runs A44A and A47 were 160 and 213 minutes, respectively.

Data are presented in Figure IX-26 for activity beyond 30 cycles, but as for Run A40 these data were not included in the correlation.

It had been noted earlier that the attrition rate tended to decline as cycling continued. Having lasted 58 cycles, Run A47 provided a good check on this notion. In the beginning the attrition rate was 1%; this dropped to 0.5% as cycling continued. Similarly, in Run A40, the attrition rate fell from 1% to 0.4% in the course of 48 cycles. All else being equal, the average attrition rate reported in this program is conservative compared to the rate which would be observed in a long run with makeup. The magnitude of the effect would depend on the make-up rate since a low make-up rate would give older bed on the average than a high make-up rate. It is possible that the process hardening procedure can be made less severe if hardening continues to occur as the stone is cycled.

G. Density of Buchanan Dolomite

As dolomite is cycled through the process it tends to densify. Data are presented in Figure IX-27 and Table IX-14 for the normalized density of hardened Buchanan dolomite as it is cycled. The data show a steady increase in density through cycle 58. Similar results had been observed with respect to Canaan dolomite.

FIGURE IX-54

RUN A49 - MOL % CaS IN EXIT SOLIDS

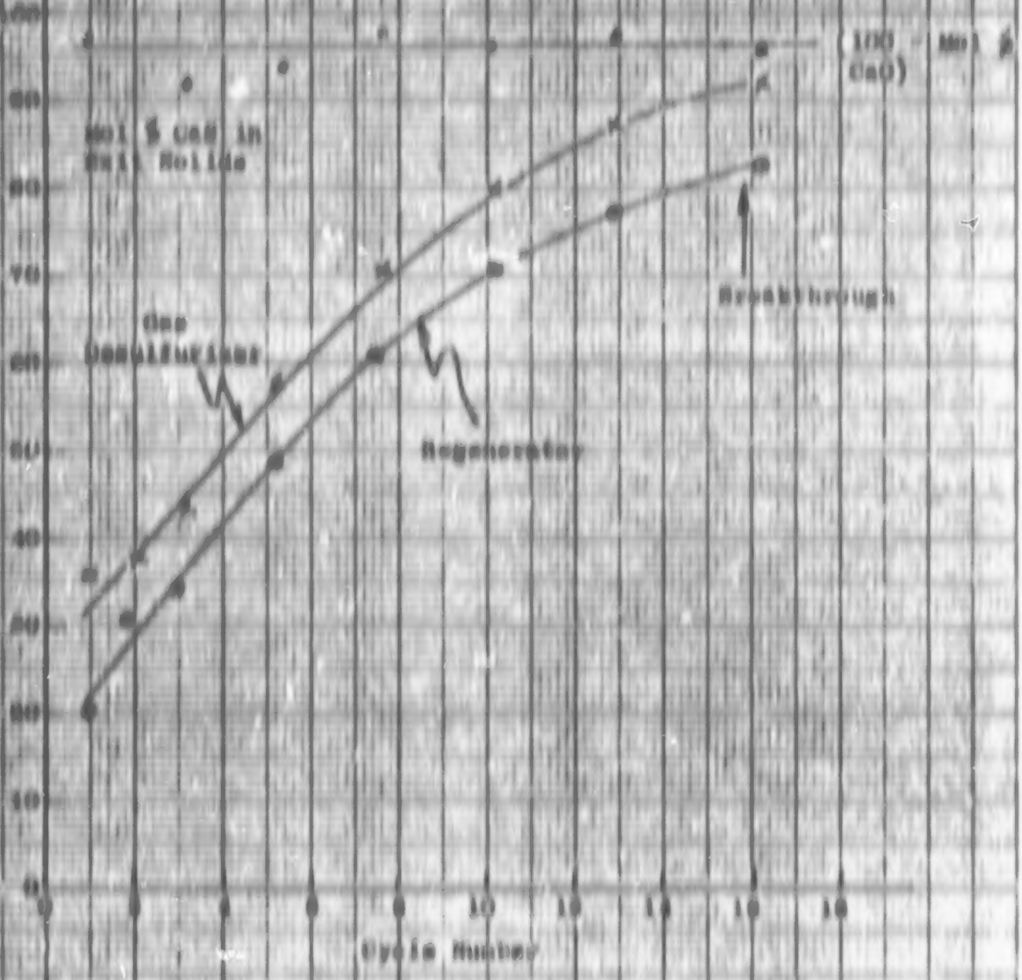


FIGURE IX-20

RUN A44A - MOL % CaS IN EXIT SOLIDS

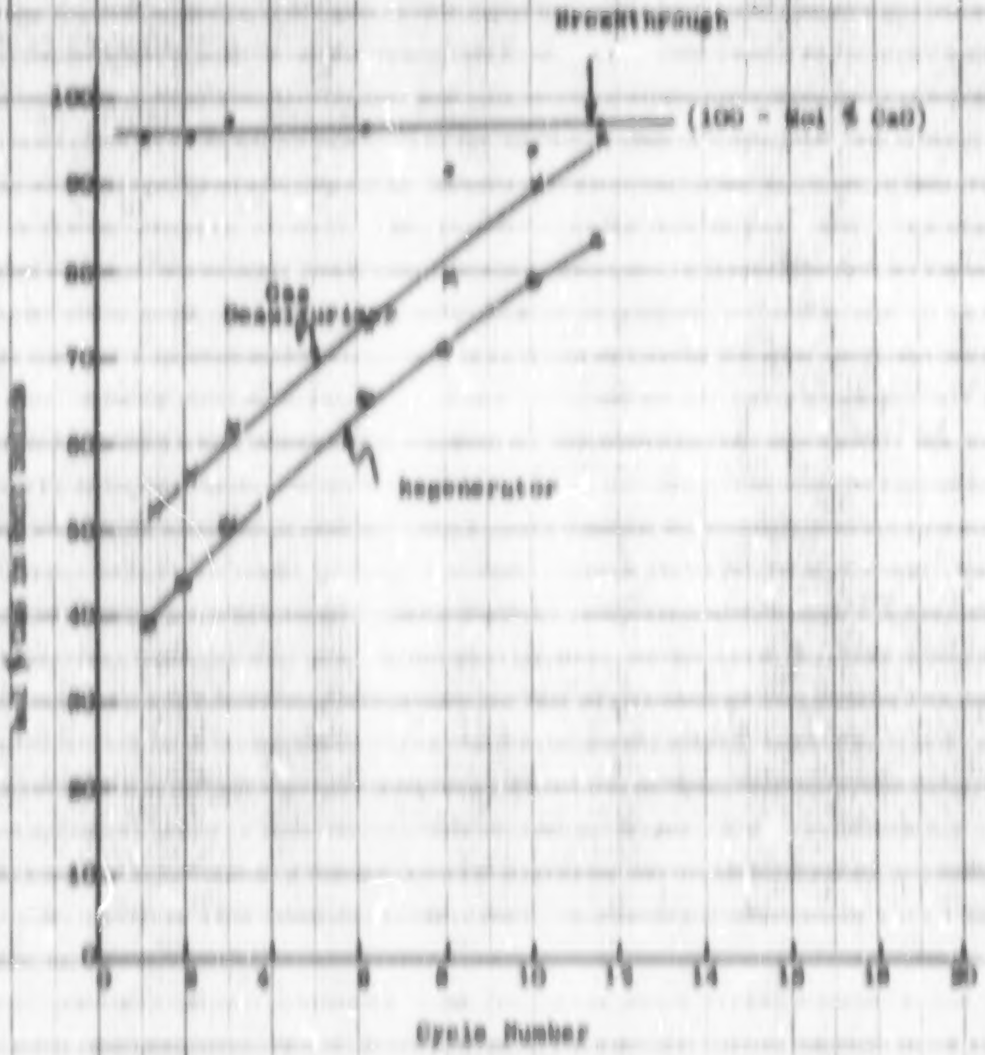
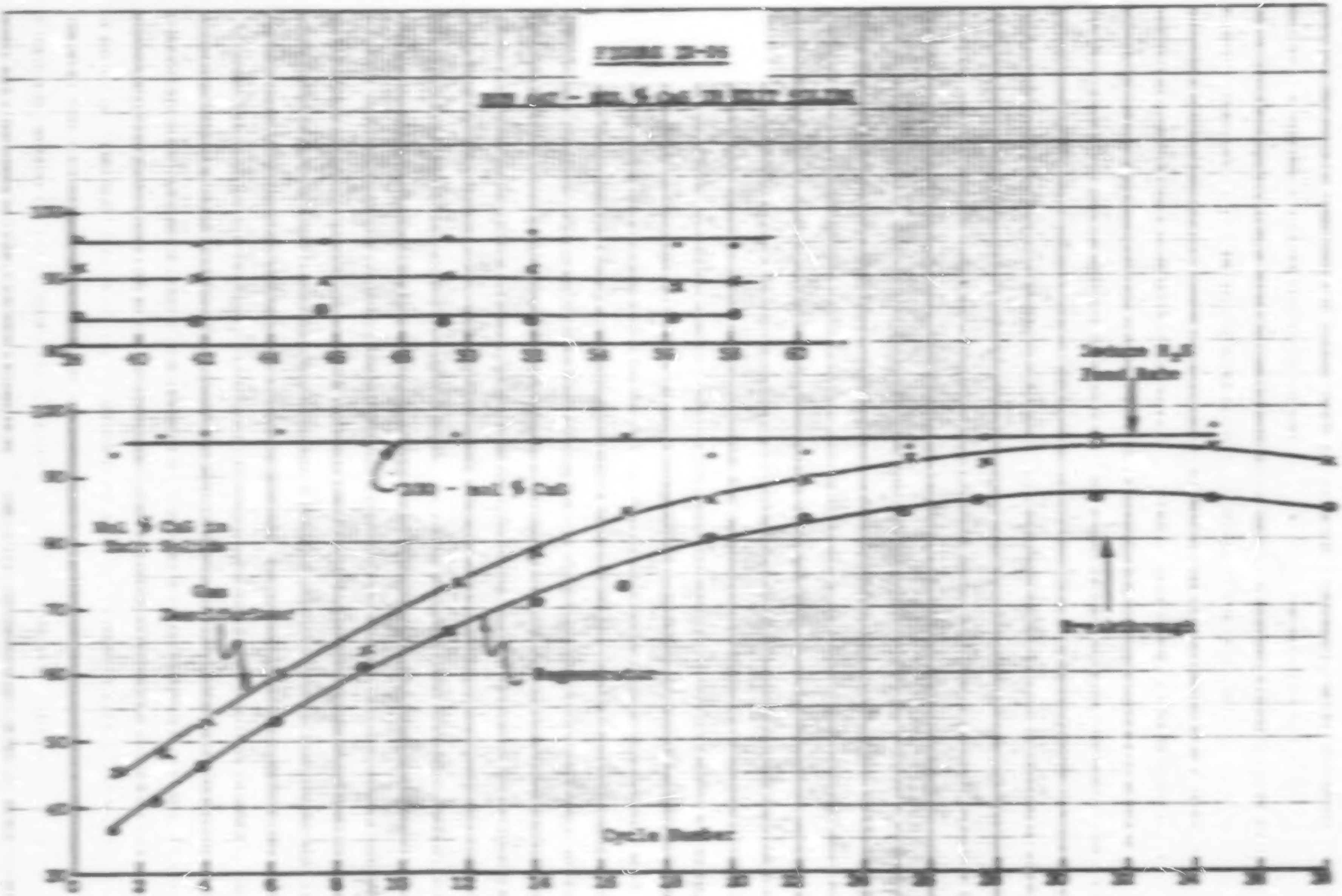


FIGURE [illegible]

[illegible]


Cycle Number
Breakthrough
Regeneration
100 - mol % CaS
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
30
40
50
60
70
80
90
100

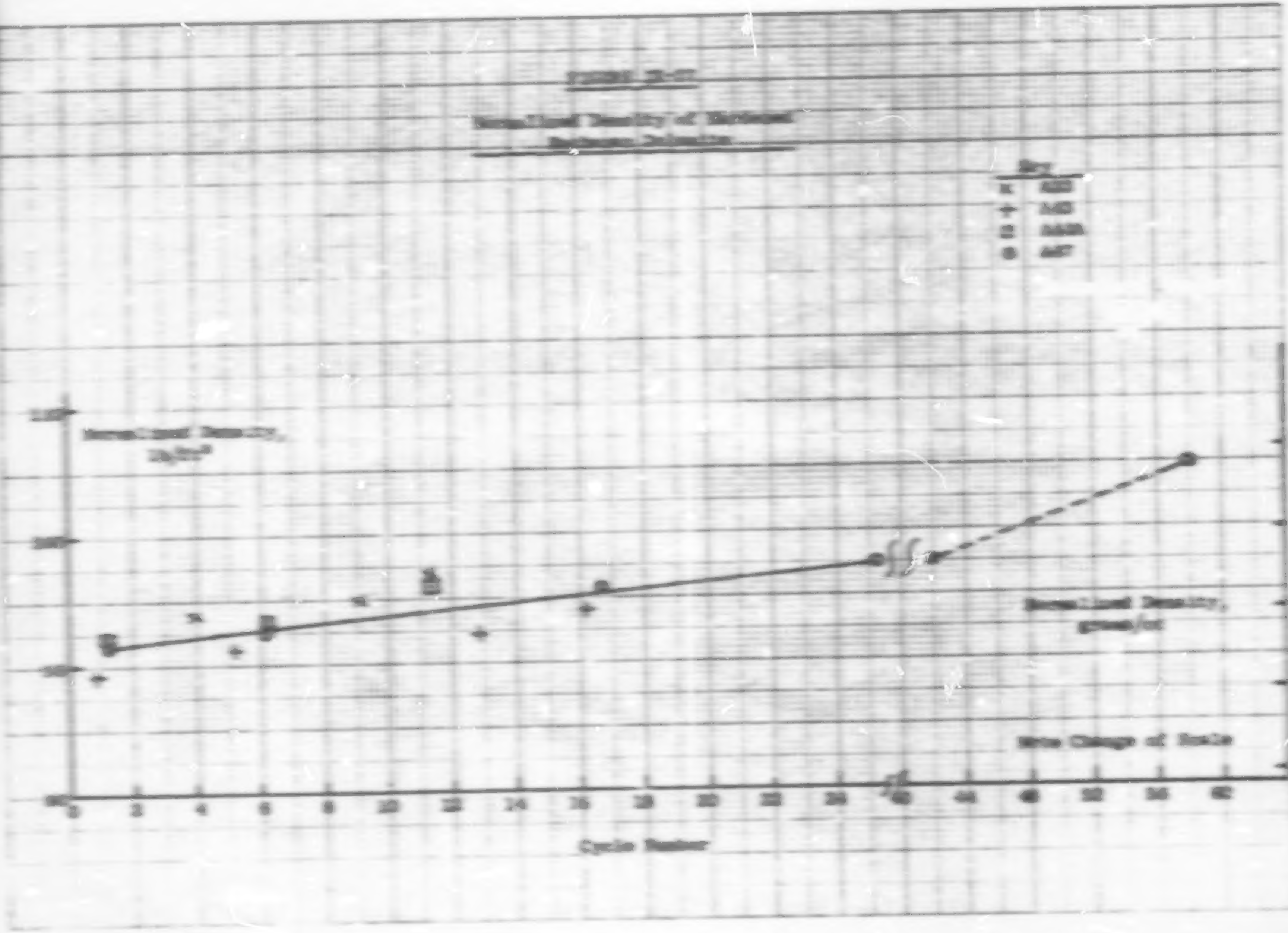

Normalized Density,
Normalized Density,
grams/cc
Note Change of Scale
1.70
1.60
1.50
1.40
1.30
0
2
4
6
8
10
12
14
16
18
20
22
24
26
40
44
48
52
56
60
Cycle Number

TABLE III-16

Density of Hardened Buchanan Dolomite

Run No.	Source	Cycle No.	$CaCO_3$	CaS	CaO	$CaSO_4$	gms/cc	lbs/ft³	Normalized Density(1) gms/cc	Normalized Density(1) lbs/ft³
433	Regenerator	3.9	65.1	29.1	1.1	4.3	2.07	129.2	1.36	81.6
		9.1	48.0	42.1	10.3	—	1.85	117.0	1.32	94.7
		11.5	38.4	55.1	6.6	—	1.95	121.9	1.35	96.0
443	Regenerator	0.9	78.2	20.6	0.8	0.5	1.99	122.9	1.42	89.2
		5.2	48.1	48.6	3.3	—	1.89	117.9	1.46	91.1
		12.9	23.1	76.9	0	—	1.82	113.3	1.49	93.2
		16.2	15.2	83.2	1.6	—	1.81	113.0	1.51	94.0
446A	Regenerator	1.2	56.4	39.3	3.0	0.4	1.965	122.6	1.48	92.3
		6.2	34.9	65.1	0	—	1.89	117.7	1.50	93.3
		11.5	13.2	83.4	3.4	—	1.86	114.6	1.54	95.9
447	Regenerator	1.2	61.5	36.8	1.6	0.3	1.96	122.2	1.47	91.5
		6.1	42.4	53.1	3.5	—	1.90	118.5	1.48	92.6
		16.7	20.9	73.3	5.8	—	1.86	116.1	1.53	95.7
		25.1	10.7	84.1	5.2	—	1.84	115.1	1.56	97.2
		41.8	10.6	83.7	5.7	—	1.85	115.5	1.56	97.6
		58.1	10.9	84.3	4.8	—	1.99	124.2	1.68	104.6

(1) Calculated by normalizing each calcium component to a CaO basis while assuming no change in sample volume.

H. Conclusions

It has been shown that a naturally soft stone can be hardened to the point where it is sufficiently attrition resistant to be used in the process. Both of the stones which we attempted to harden were successfully processed; there were no failures. This success means that plant siting will not be severely constrained by the need to have a rather particular type of dolomite in the vicinity. Dolomites are rather widespread and it is likely that a suitable stone which can be hardened can be found nearby.

Three different batches of Tymochtee dolomite were hardened. It was found that there was some loss of activity in two of the batches, but the other displayed an activity slightly better than that of Canaan dolomite, the base case stone. Buchanan dolomite was hardened with some loss of activity. However, it is likely that the hardening conditions were somewhat more severe than was needed, and that the stone can be hardened and still display an activity comparable to that of Canaan stone.

It was found that the severity of the hardening step affects both activity and attrition resistance but in opposite directions. Tymochtee dolomite run at 982°C (1800°F) was very hard but displayed rather reduced activity. An optimal condition was found at 871-927°C (1600-1700°F) for the oxidation step with about 20% conversion. Runs made at 4% and 0% conversion showed excessive attrition rates. Using Buchanan dolomite, it was found that 35% conversion gave a very hard stone with reduced activity compared to 15% sulfidation which gave a high activity stone with poor attrition resistance.

For regeneration activity, there was no effect noted of particle size over the range of 20 x 28 to 35 x 48 Tyler mesh. The effect on attrition was somewhat more difficult to evaluate due to the carryover problems caused by insufficient disengaging height, but generally the rate was not different from the 35 x 48 mesh stone.

It is not known at this time why the different batches of Tymochtee stone showed varying activity. This was not observed for either Buchanan or Canaan dolomite.

X. BATCH SULFIDATION AND REGENERATION EXPERIMENTS

A. Batch Sulfidation Studies

A total of 45 batch runs were made to study variables affecting operation of the gas desulfurizer. Base conditions for the batch sulfidation study are given in Table X-1. These were essentially the same as for continuous runs. Properties of feedstocks employed in both the sulfidation and regeneration studies are shown in Table X-2. For sulfidation, a batch of fresh 28 x 35 Canaan dolomite was one of the feedstocks. Another was prepared by riffling together the regenerator beds of Runs A30A, A31 and A33A, all made with Canaan dolomite. These runs were carried out to 33, 37 and 30 cycles, respectively. Tymochtee II dolomite was the third feed.

The procedure was to fill the bed with the programmed charge, equilibrate with respect to temperature and gas flows, and then start feeding H_2S. The outlet H_2S concentration was followed on the ultraviolet analyzer, and upon breakthrough the H_2S flow was shutoff. The cold leg of the reactor (L-5) was purged of solids in order to get an uncontaminated sample of the bed. As the H_2S fed beyond the breakthrough point could be considerable, the $CaCO_3$ content of the stone was corrected from the assayed value using a sulfur balance based on the recorded analyzer output. The gas residence time and bed height were calculated for each run based on the weight and density actually observed.

The amount of excess $CaCO_3$ required in the bed to prevent breakthrough of H_2S was correlated as a space rate, mols H_2S/hr-mol of $CaCO_3$ remaining at 0.10% H_2S in the dry exit gas. The level of 0.1% was chosen for operational convenience. Once breakthrough occurred, the H_2S concentration rose rapidly, and the time to go from 0.05% to 0.20%, for example, was short. The data for all the cases are presented in Table X-3, and in a statistical layout in Table X-4. The data tended to scatter, but the space rate held constant as the following variables were changed: fresh versus cycled stone, bed depth from 4 to 17 inches, particle size from 28 x 35 to 35 x 48 mesh, and mol % inlet H_2S from 0.3% to 1.1%. Only temperature was found to have an effect; the average space rate increased from 1.9/hr to 3.0/hr in going from 871 to 927°C (1600-1700°F). Analysis of the data followed the procedures outlined by Hicks.(10) The analysis of variance (ANOVA) is given in Table X-5 for the runs in which a variable effect was found.

By way of comparison, Westinghouse(11) examined the reaction under similar conditions using a thermogravimetric (TG) experimental system. They reported the rate of reaction to decrease by about 6% in going 871 to 927°C (1600-1700°F) and to decrease by 3% for each sulfidation-regeneration cycle. Rate of sulfidation increased with decreasing particle size over the range of about 28 to 8 Tyler mesh. The Westinghouse results do not concur with those reported here, but the dependent variables differed, the independent variables were changed over a narrow range, most effects were small, and different experimental techniques were used. Pending further studies, the Conoco results are assumed to be correct since experimental conditions more closely simulated the process conditions and fluidized bed mechanics of interest to our process.

It was found that the concentration of H_2S in the outlet gas varied with conditions even when there was an excess of $CaCO_3$ present in the bed. The data for percent H_2S prior to breakthrough are presented in a statistical layout in Table X-6. The ANOVA tables for the various data sets are given in Table X-7.

TABLE 3-1

Conditions for Batch Sulfidation Runs

System Pressure: 15 atm (206 psig)

Run Number	A83-A87	A87-A95	A99-A106	A109-A116	A117-A119
Temperature, °C	871 (1600°F)	871 (1600°F)	899 (1650°F)	927 (1700°F)	927 (1700°F)
Type of Dolomite	Canaan 3	Canaan 3	Canaan 3	Canaan 3	Tymochtee 22
Acceptor Size Consist, Tyler Mesh	28 x 65	35 x 48	35 x 48	35 x 48	35 x 48
Input, SCFH (1)					
Recycle to Bed					
H_2	280	246	280	80	80
N_2	37	11	11	16	16
CO	35	4.6	3.5	8	8
CO_2	40	22	12	27	27
N_2	18	18	29	30	30
H_2S	38	46	42	120	120
Purges (CO_2) to Bed	1.3-4.3	0.9-3.0	0.9-3.0	0.9-3.0	3.0
Purges (N_2) above Bed	5	5	5	5	5
	25	25	25	25	25
Output					
Exit Gas Rate, SCFH (dry basis)	315	132	101	220	221
Composition, Mol %					
H_2	27	3.4	3.5	4	4
CO	19	10.5	11.0	8	8
CO_2	22	21	29	13	13
N_2	32	65	56	75	75
H_2S	—	—	—	—	—
Outlet Gas, Top of Bed					
Composition, Mol %					
H_2O	8	4.8	4.6	5	5
H_2	16	3.4	3.5	4	4
CO	18	10.6	11	8	8
CO_2	17	21	29	13	13
N_2	40	60	51	69	69
H_2S	—	—	—	—	—
Flow Rate, SCFH, Top of Bed	430	260	250	272	272
Fluidizing Velocity, ft/sec	0.52	0.38	0.38	0.41	0.42

(1) Input is given after shift reaction and hydrolysis of COS have taken place.

TABLE [illegible]

[illegible]

[illegible]	[illegible]	[illegible]			[illegible]		[illegible]					
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	100	0	0	—	—	[a]	—	—	—	—	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	—	—	—
[illegible]	[illegible]	100	0	0	—	—	—	—	100	—	—	—

[a] [illegible]

TABLE A-4

Mols H_2S Fed/hr Per Mol $CaCO_3$ Remaining at 0.10% H_2S in Exit Gas

X-4A Runs A83-A87

Bed Depth, inches	16.5-17.5		10.4-10.5	7.3-7.8	
Age of Stone	Fresh	Cycled	Fresh	Fresh	Cycled
Mol % H_2S, Inlet					
0.34	1.87	2.04	3.43	3.06	2.43
0.64	2.93	2.37	3.06	2.40	2.70
1.06	1.63	2.83	3.12	1.75	2.33*

* Estimated by a sum of squares minimization technique recommended by Hicks.(11)

X-4B Runs A53-A61, A87-A95

Bed Depth, inches	16.0-17.0		9.2-10.0		4.3-7.6	
Size Consist, Tyler mesh	35 x 48	28 x 35	35 x 48	28 x 35	35 x 48	28 x 35
Mol % H_2S, Inlet						
0.3	0.91	1.87	1.67	3.43	1.04	3.06
0.6	1.34	2.93	1.10	3.06	0.99	2.40
1.0	3.29	1.63	4.08	3.12	1.38	1.75

X-4C Runs A87-A95, A98-A106, A108-A116

Bed Depth, inches	16.0-17.0			9.2-10.0			4.3-4.8		
Temperature, °F	1600	1650	1700	1600	1650	1700	1600	1650	1700
Mol % H_2S, Inlet									
0.3-0.4	0.91	1.59	1.65	1.07	2.10	2.43	1.04	2.08	3.39
0.6-0.7	1.34	2.87	3.19	1.10	3.28	3.88	0.99	0.95	3.40
1.0-1.1	3.29	2.43	4.10	4.09	2.33	3.39	1.38	1.27	1.93

TABLE E-5

ANOVA for Mols H_2S/hr-Mol $CaCO_3$ at Breakthrough
Runs A87-A95, A96-A104, A105-A113

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Level of Significance
Mol % H_2S, Inlet	2	3.7638	1.8819	2.17	< 90%
Bed Depth	2	4.1965	2.0983	2.42	< 90%
Temperature	2	6.9605	3.4803	4.02	> 95%
Error	20	17.3250	.8663		
Total	26	32.2459			

TABLE X-9

Mol % H_2S in Dry Outlet Gas
With Excess $CaCO_3$ Remaining in the Bed

X-9A Runs A62-A67

Bed Depth, inches	16.5-17.5		10.4-10.5	7.3-7.8	
Age of Stone	Fresh	Cycled	Fresh	Fresh	Cycled
Mol % H_2O, Inlet					
0.74	0.04	0.05	0.04	0.05	0.05
0.84	0.05	0.04	0.05	0.06	0.06
1.06	0.05	0.08	0.06	0.06	0.06*

* Estimated by a sum of squares minimization technique recommended by Hicks.(11)

X-9B Runs A52-A61, A87-A95

Bed Depth, inches	16.0-17.0		9.3-10.9		4.3-7.8	
Size Consist, Tyler mesh	35 x 48	28 x 35	35 x 48	28 x 35	35 x 48	28 x 35
Mol % H_2O, Inlet						
0.3	0.04	0.04	0.04	0.04	0.07	0.06
0.6	0.04	0.05	0.05	0.04	0.08	0.06
1.0	0.04	0.05	0.05	0.05	0.08	0.08

X-9C (Mol % H_2O-H_2S Equilibrium)
in Dry Outlet Gas with Excess $CaCO_3$ Remaining in Bed
Runs A87-A95, A96-A100, A106-A116

Bed Depth, inches	16.0-17.0			9.8-10.9			4.3-4.8		
Temperature, °F	1600	1650	1700	1600	1650	1700	1600	1650	1700
Mol % H_2O, Inlet									
0.3-0.4	0.01	0.01	0.01	0.01	0.02	0.01	0.04	0.04	0.01
0.6-0.7	0.01	0.02	0.01	0.02	0.02	0.01	0.02	0.05	0.03
1.0-1.1	0.01	0.02	0.01	0.02	0.02	0.01	0.06	0.06	0.03

TABLE X-7

ANOVA For Mol % H_2S in Dry Outlet Gas

Data were coded by multiplying by 100

X-7A Runs A53-A60, A65-A67

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Level of Significance
Mol % H_2S, Inlet	2	2.4608	1.2304	3.74	> 90%
Bed Depth	1	2.4571	2.4571	7.46	> 95%
Age of Stone	1	0.1704	0.1704	< 1	Nil
Error	6	1.9762	0.3294		
Total	10	7.0644			

X-7B Runs A53-A61

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Level of Significance
Mol % H_2S, Inlet	2	2.8889	1.4444	13.00	> 95%
Bed Depth	2	1.5556	0.7778	7.00	> 95%
Error	4	0.4444	0.1111		
Total	8	4.8889			

X-7C Runs A53-A61, A87-A95

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Level of Significance
Mol % H_2S, Inlet	2	3.444	1.722	2.02	< 90%
Bed Depth	2	14.777	7.389	8.67	> 99%
Particle Size	1	0.500	0.500	< 1	Nil
Error	12	10.223	0.852		
Total	17				

X-7D Runs A87-A95, A98-A106, A108-A116

Factor	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Level of Significance
Inlet H_2S	2	3.6297	1.8149	2.54	< 90%
Bed Depth	2	34.7408	17.3704	24.30	> 99%
Temperature	2	9.4074	4.7037	6.58	> 99%
Error	20	14.2962	0.7148		
Total	26	62.0741			

The following independent variables were judged to have no effect on outlet H_2S concentration: age of stone, particle size over the range 28 x 35 to 35 x 48 mesh, and inlet H_2S concentration over the range 0.3% to 1.1%. The result on inlet H_2S concentration is not as certain as the others, since one of the data subsets (Runs A53-A61) did show an effect at the 95% significance level. For all other subsets, the effect was less than the 90% level.

The effect of decreasing bed depth was to increase the outlet H_2S before breakthrough. Increasing the temperature in the range of 871 to 927°C (1600-1700°F), reduced the outlet H_2S concentration. Deeper beds and higher temperature gave closer approach to equilibrium. It is noted that in deep beds (>9 inches), the approach to equilibrium with within 0.02%, about the limit of accuracy of the H_2S analyzer. In addition, the closest approach was observed at 1700°F, followed by 1600°F, followed by 1650°F, and this is an anomalous ordering. Pending studies capable of improved accuracy, the outlet H_2S concentration will be assumed to be at the equilibrium level for purposes of the process design.

Runs A117 to A119 were made with Tymochtee 11 dolomite rather than with Canaan stone. Table X-3 shows that the H_2S concentration before breakthrough was about the same as for Canaan stone, but the space rate at breakthrough was much higher. The cause of the observed difference is not known.

The results of the study are consistent with a model of very fast reaction in which the exit gas is close to equilibrium. Although tripling the inlet gas concentration would be expected to increase the outlet concentration, when combined with the equilibrium base of 0.02%, the observed effect would be small. Decreasing the bed depth would be expected to have an effect due to gas bypassing.

The fact that age of the $CaCO_3$ had no effect is consistent with previous conclusions, and again confirms a key feature of the process.

Overall, the batch runs did not give results as good as those from continuous runs. The H_2S concentration prior to breakthrough was slightly higher, and breakthrough occurred with more $CaCO_3$ remaining in the bed. The reasons for the differences are not understood at this time. Perhaps the regenerated material falling into the bed from above gives some countercurrency to the continuous system.

A complicating factor in the analysis was that the H_2S feed was made from CS_2. It had been shown that all the CS_2 is hydrolyzed to H_2S in a full bed of inert MgO (magnorite). However, the rate of hydrolysis and the rate of the shift reaction which produced the water may become limiting factors in the very short beds which were employed in this study. It was assumed that sulfur entered the bed in the form of H_2S with the understanding that the runs with four-inch beds represent a limiting case of how short a residence time can be investigated with the existing equipment.

B. Batch Regeneration Study

Base conditions for the regeneration study are given in Table X-8. The gas desulfurizer beds of the sulfidation study were combined to give two feedstocks consisting of sulfided fresh stone and sulfided cycled stone, respectively. Detailed results and variables pertaining to regeneration runs are presented in Table X-9. The main study involved temperatures of 649, 704 and 760°C (1200, 1300 and 1400°F) with full (36 inch) and one-half (18 inch) beds and fresh and recycled stone.

TABLE 5-5

Typical Conditions for Batch Regeneration Runs
System Pressure: 15 atm (206 psig)

Run Numbers	A68-A78	A80, A81
Temperatures, °C	649-760 (1200-1400°F)	816, 871 (1500, 1600°F)
Nominal Solids Residence Time, hours	8	8
Input, SCFH		
Recycle to Bed	0	0
H_2O	70	60
N_2	8	7
CO	0	0
CO_2	135	117
Purges (CO_2) to Bed	10	10
Purges (N_2) above Bed	0	0
Purges (CO_2) above Bed	15	15
Output		
Exit Gas Rate, SCFH (dry basis)	165	145
Composition, Mol %		
H_2	2.3	1.6
CO	2.6	3.2
CO_2	93	94
N_2	0.7	0.2
H_2S	(1)	(1)
COS	(2)	(2)
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	35	38
H_2	1.6	1.1
CO	1.9	2.3
CO_2	60	60
N_2	0.5	0.2
H_2S	(1)	(1)
COS	(2)	(2)
Flow Rate, SCFH, Top of Bed	250	205
Fluidizing Velocity, ft/sec	0.6-0.7	0.6

(1) See detailed data for each run.
(2) Usually 3-5% of the H_2S.

The procedure was to fill the bed with the programmed charge and then to turn on the steam feed. The runs were continued for eight hours or until there was no longer any change in H_2S content, whichever came first. As a rule, the H_2S concentration at the end of the run was less than 0.10% on a dry basis. The cold leg of the reactor (L-8) was purged of solids prior to taking a sample of the bed.

The data for percent regeneration are listed in Table X-10. By inspection, the effect of temperature seemed to be different for cycled stone and fresh stone. A temperature times age interaction term, TxA, was therefore included in the ANOVA, Table X-11. The effects of temperature, bed depth, age of stone, and temperature times age were all found to be significant at the 1% level. The TxA effect showed that increasing temperature improved conversion more for cycled stone than for fresh stone.

The effect of bed depth was unusual. It was expected that since the deeper bed ran at an H_2S outlet concentration closer to equilibrium, there would be less driving force for reaction and the regeneration conversion would be lower. In all six test pairs exactly the opposite was found. The runs with the deeper beds, i.e., higher H_2S outlet concentration, gave higher conversions. This is consistent with earlier conclusions that increasing the H_2S concentration does not adversely affect conversion in the regenerator.

Figure X-1 is an attempt to correlate the factors contributing to approach to equilibrium in the outlet gas. It was assumed that the more mols of solid reactants per mol of gas, the closer equilibrium is approached; temperature is an obvious parameter. The data in Figure X-1 follow the expected trend, but no simple functional correlation is discerned.

Two additional exploratory runs were made at 816 and 871°C (1500 and 1600°F) with cycled stone from the two 1300°F regenerator runs, A75 and A76. Conversions based on the original sulfided feed were 67% and 81% at 1500 and 1600°F, respectively. Although the equilibrium H_2S concentration is low at these temperatures, it was thought that a reactivation process might be feasible if a slipstream of stone could be treated at an elevated regeneration temperature. It turned out that the stone could not be so reactivated, and details are discussed in Section X-D.

C. Regeneration Kinetics

Regeneration kinetics were examined by recording the H_2S concentration in the exit gas as a function of time as the runs progressed. The total mols of H_2S produced were normalized to match the total mols of CaS reacted, and conversion as a function of time was then plotted. These results are presented in Figures X-2 to X-5 in the form of (1 - X) versus time, where X is the fractional conversion of the CaS feed.

In all cases, the rate continuously decreased. It appeared that the reaction would eventually cease while there was still considerable CaS left. This is consistent with the notion that much of the CaS is simply unreactive. The initial reaction rate was faster for fresh stone than for cycled stone at all temperature levels. Additionally, the rate seemed to slow sooner for the cycled stone. The curves also show that the effect of bed depth is present even at the early stages of all reactions; the deeper beds had a higher reaction rate at all times.

TABLE X-10

Regeneration Results - Percent Regeneration

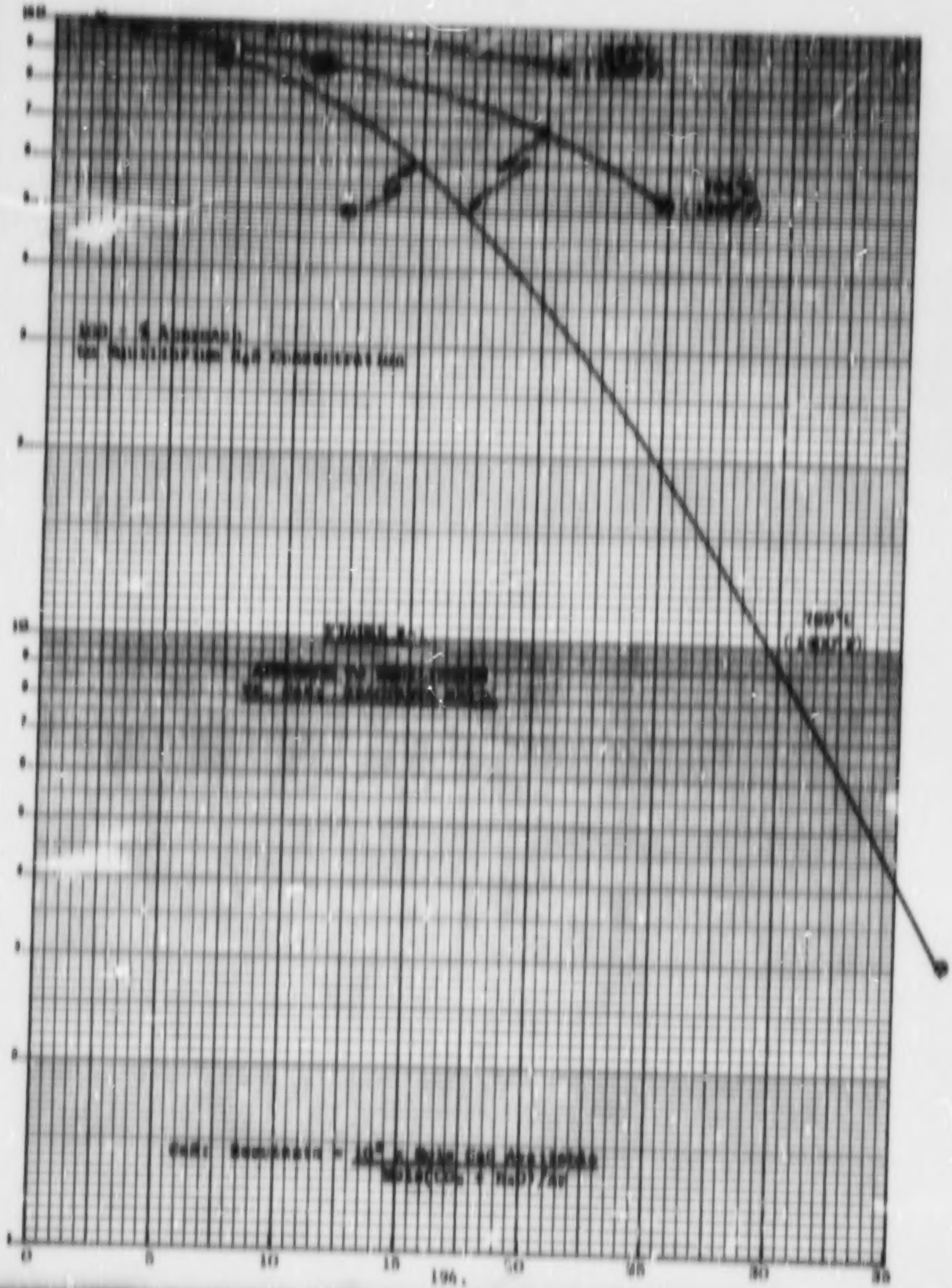
Bed Depth Age of Stone Temp., °F (°C)	Full Fresh	Full Cycled	2/3 Cycled	1/3 Fresh	1/3 Cycled
1200 (649)	61.9	14.5		57.6	10.9
1300 (704)	75.8	31.8		71.8	28.0
1400 (760)	80.8	58.4		78.3	48.8
1500 (816)			87.1		
1600 (871)			81.0		

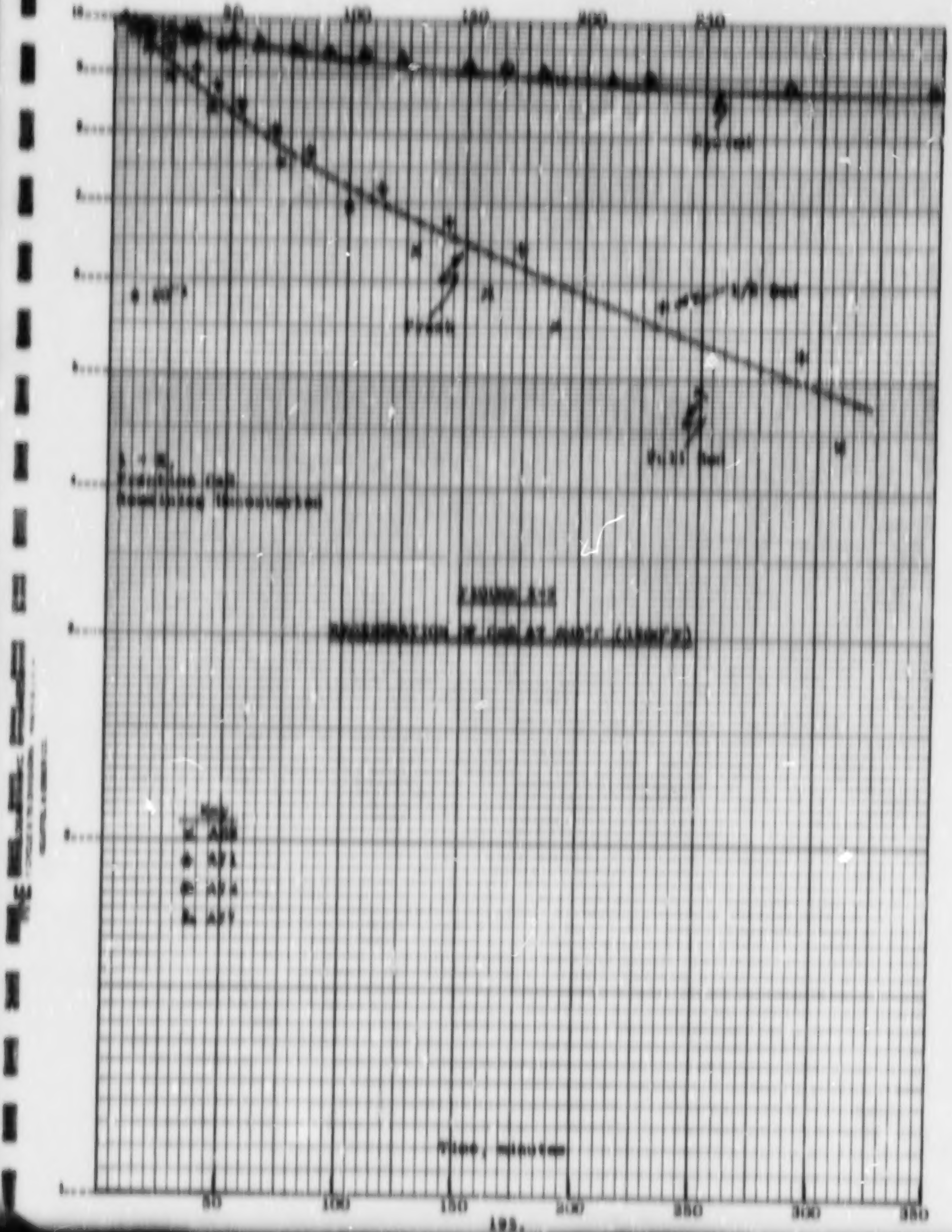
TABLE X-11

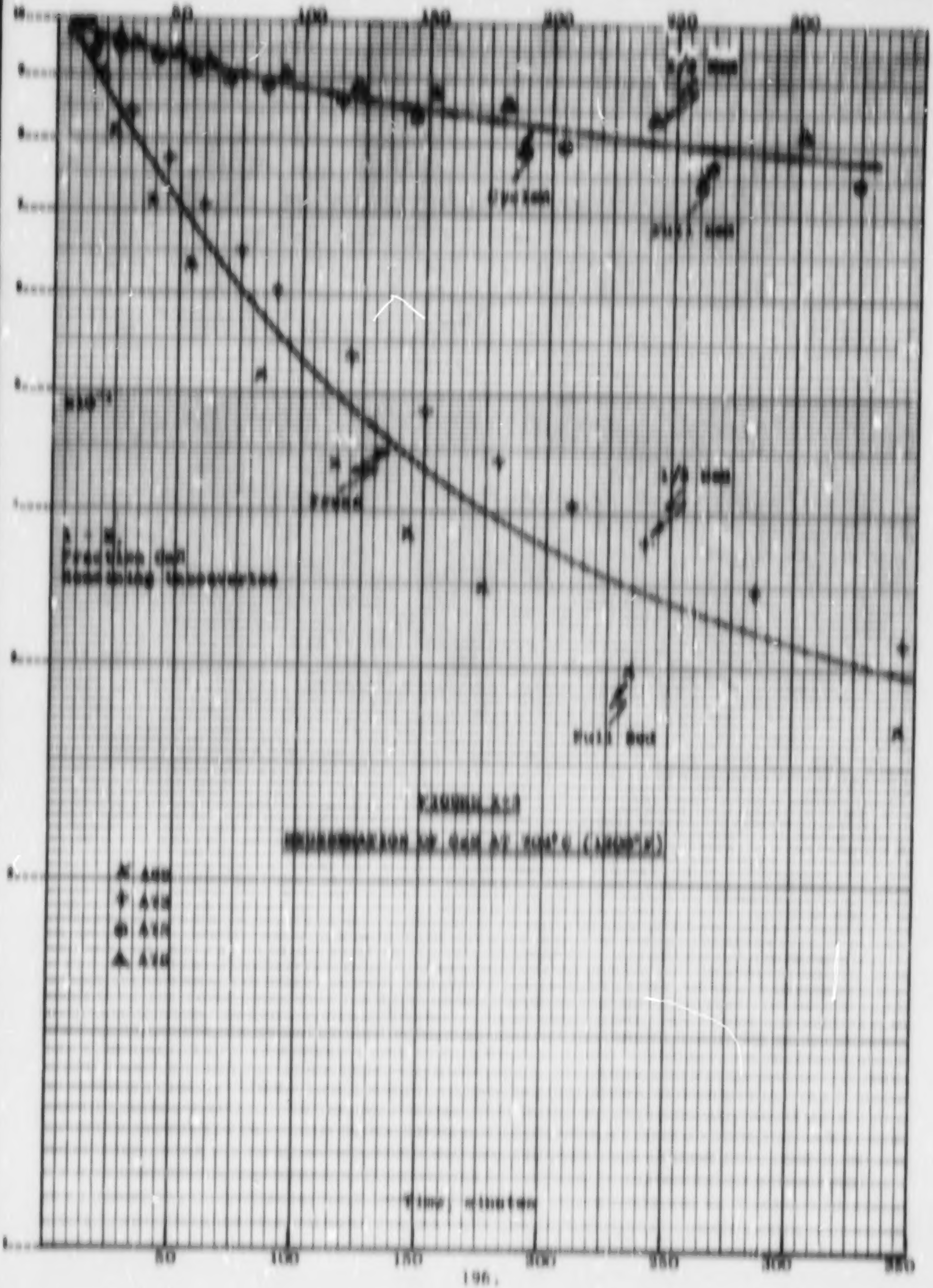
ANOVA for Percent Regeneration

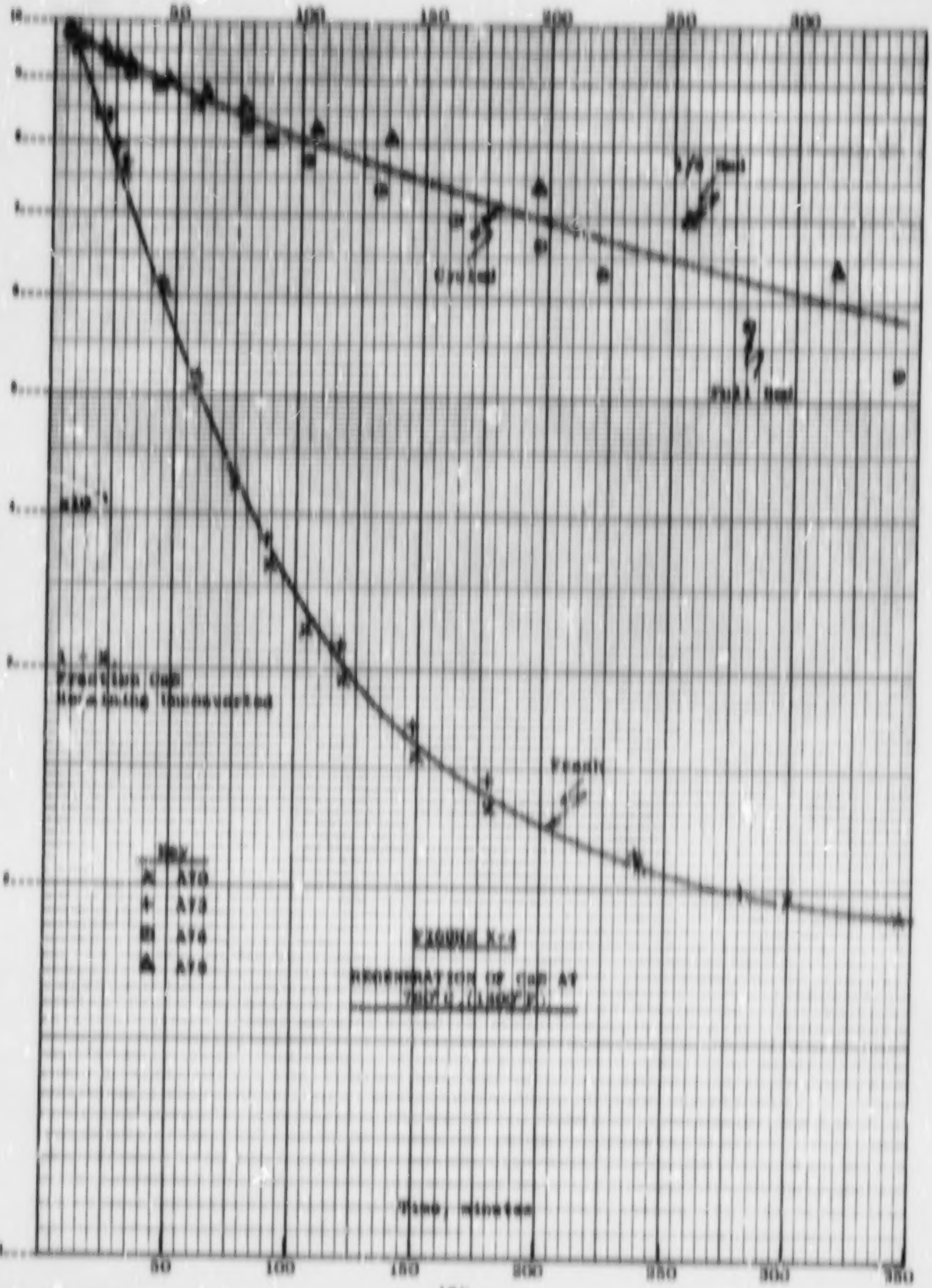
Data for 1500°F and 1600°F were excluded
Data were coded by multiplying by 0.10

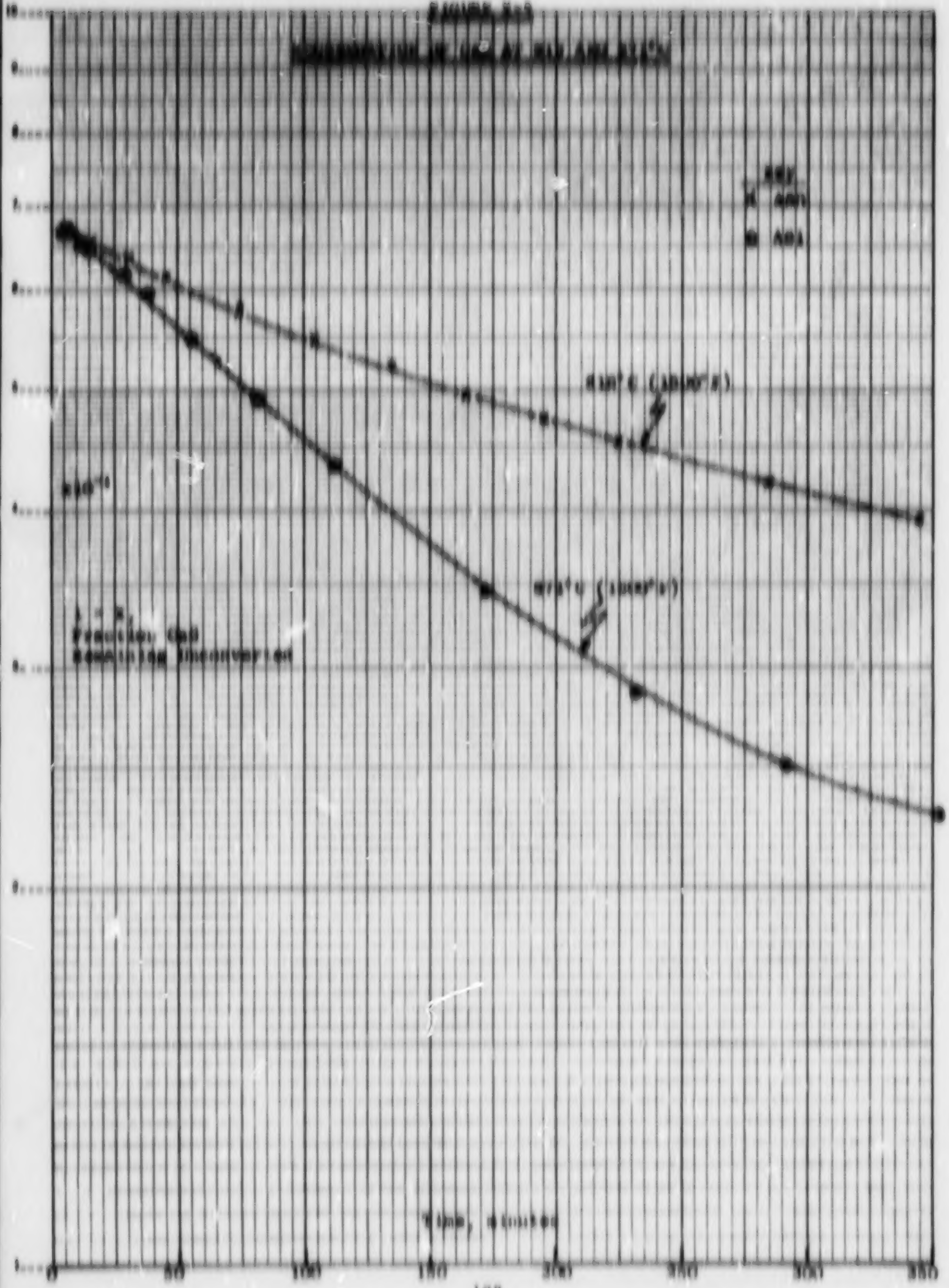
Factor	Degrees of Freedom	Sum of Squares	Mean Square	F Ratio	Level of Significance
Temperature	2	15.848	7.924	122.3	> 99%
Bed Depth	1	1.056	1.056	16.3	> 99%
Age of Stone	1	50.758	50.758	783.3	> 99%
T x A	2	1.684	0.842	13.0	> 99%
Error	6	0.389	0.0648		
Total	11	69.735			


100
10
0
5
10
15
20
25
30
35


50
100
150
200
250
50
100
150
200
250
300
350


50
100
150
200
250
300
Cycles
Fresh
Field Gas
Fraction Gas
Remaining Undecomposed
Time, minutes
50
100
150
200
250
300
350


50
100
150
200
250
300
10
1
Cycles
Run
Time, minutes
50
100
150
200
250
300
350


[illegible]
KEY
x10⁻¹
Fraction
Remaining Unconverted
Time, Minutes
10
1
0
50
100
150
200
250
300
350

While the reaction kinetics are clearly very complicated, they may be approximated by a simple first order rate constant for the short times (about an hour) of interest to the process. The reaction model would then be:

$$Kt = -\ln (1 - X)$$

where K = rate constant, hr^{-1}, whose function of H_2S concentration is yet to be determined.
t = time, hours.
and X = fractional conversion of the CaS fed.

The value of K was taken from the slope of the data from 5 to 60 minutes in Figures X-2 to X-4, and is tabulated in Table X-12. The data of Table X-12 are plotted in Figure X-6. The activation energies for cycled and fresh stone are shown to be the same, about 19 kilocalories.

The kinetic mechanism proposed here allows one to calculate the effect of changing conditions of temperature or residence time upon fractional conversion of CaS (percent regeneration).

D. Cyclic Sulfidation and Regeneration

Run A85 - Cycling of Reactivated Dolomite

Run A85 constituted two sulfidation-regeneration cycles on the combined product of Runs A80 and A81. In these runs cycled Canaan dolomite was regenerated for 8 hours at 816 or 871°C (1500 or 1600°F). A highly regenerated product (high $CaCO_3$ content) was obtained. Run A85 was set up to determine the performance of the regenerated stone, i.e., whether any reactivation took place along with regeneration. Sulfidation conditions were the same as for Runs A52-A67 described earlier. Regeneration was at 704°C (1300°F) with the usual 65% CO_2, 30% H_2O composition.

The history of the stone and the result of Run A85 are presented in Table X-13. In two attempts at sulfidation, breakthrough occurred immediately and almost no $CaCO_3$ reacted. Although a considerable quantity of $CaCO_3$ had been formed in the high temperature regeneration, it displayed very poor reactivity.

The data in Table X-13 show a decline in "CaO" as the stone is cycled through the long regeneration at 704°C (1300°F), and a further decline after regeneration at 817 and 871°C (1500 and 1600°F). The "CaO" level started to rise upon cycling in the normal sulfidation-regeneration mode. It is possible that the rigorous regeneration conditions encouraged recarbonation of the inert "CaO". However, it is noted that the data in Table X-9 do not show any effect of temperature on "CaO' content over the range 649-760°C (1200-1400°F).

Run A124 - Reactivated Stone at Calcining Conditions

Run A124 consisted of a single sulfidation and regeneration of Run A85 material, stone which had been regenerated at 817-871°C (1500-1600°F), and which then displayed poor reactivity toward H_2S. The stone was sulfided at 927°C (1700°F) under calcining conditions. High reactivity toward H_2S was obtained. Upon regeneration, only 11% relative conversion of CaS to $CaCO_3$ occurred. It is

TABLE E-12

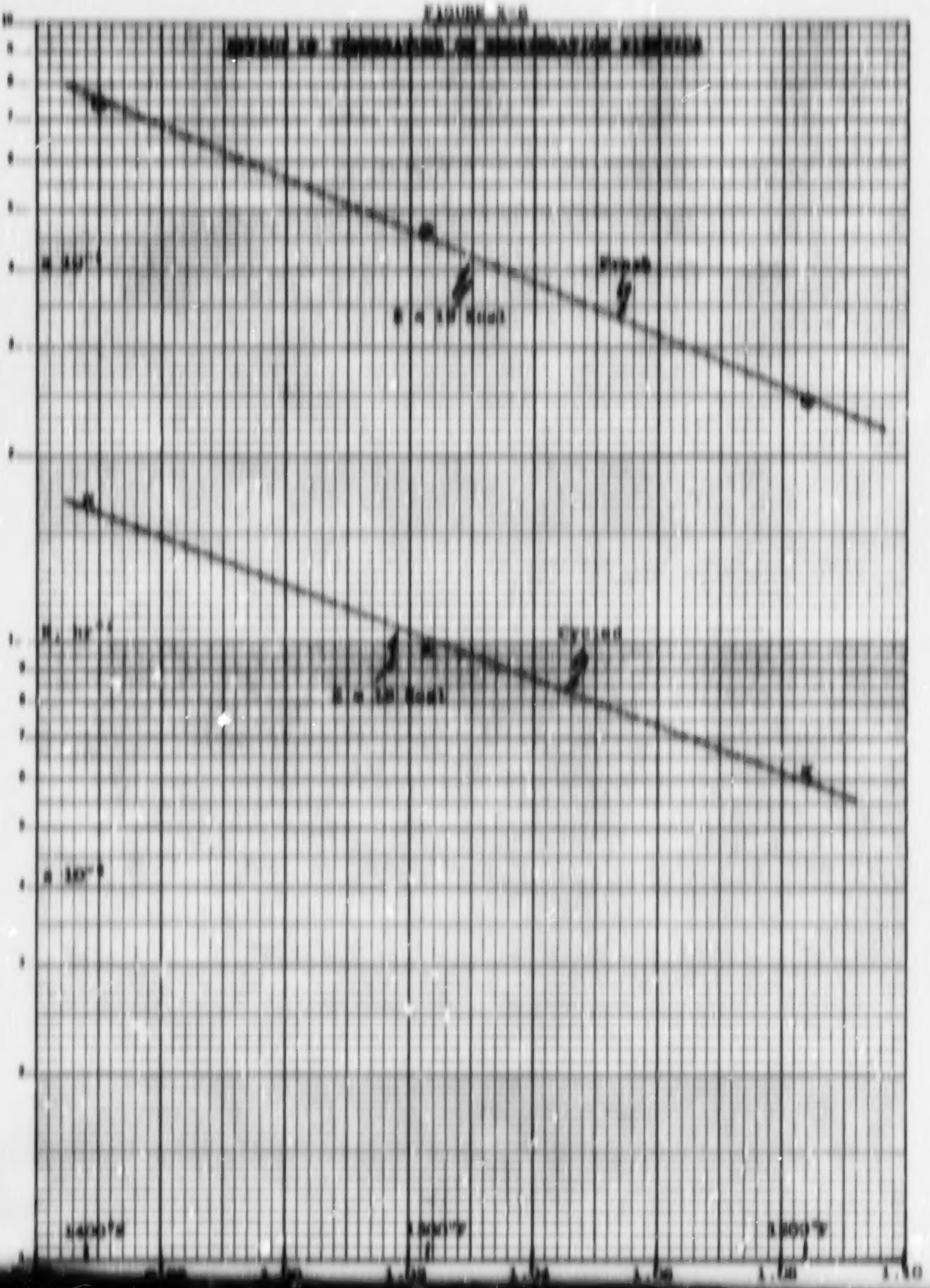
Initial Rate Constants for Regeneration Kinetics

System Pressure: 15 atm
Feed: 35% H_2O, 60% CO_2, 5% H_2

Temperature, °C (°F)	K, hr^{-1}	
	Cycled	Fresh
649 (1200)	.063	.247
704 (1300)	.098	.488
760 (1400)	.170	.747

[illegible]

[illegible]



1400°F
1600°F
1800°F

TABLE B-13

History and Cycling Results for Reactivated Dolomite

Material Description	Mol % CaCO$_3$	Mol % CaS	Mol % CaO
A. History			
Cycled Canaan Dolomite Feed Composited from Runs A20A, A21, A30A	24.2	69.6	6.2
Sulfided Stone Composited from Runs A53-A61	12.8	82.0	5.2
Stone Regenerated at 704°C (1300°F), Runs A75 and A76	38.6	58.5	3.0
Stone further Regenerated at 816 and 871°C (1500 and 1600°F), Runs A80 and A81	73.4	26.0	0.6
B. Cycling Results - Run A82			
Sulfidation No. 1 871°C, till breakthrough	67.9	32.1	0
Regeneration No. 1 704°C, 60 minutes	71.8	27.9	0.3
Sulfidation No. 2 871°C, till breakthrough	70.8	27.7	1.5
Regeneration No. 2 704°C, 60 minutes	72.8	24.0	3.2

concluded that stone reactivated at elevated temperatures would be active in the CaO form, but that subsequent regenerations would give the same conversions as for the original deactivated material. Run conditions are given in Tables X-14 and X-15.

Run A86 - Cycling of Dolomite Regenerated at 760°C (1400°F)

The results of Run A85 implied that $CaCO_3$ produced by regeneration at high temperatures might be unreactive. Preliminary results obtained at The City University of New York[18] also indicate that unreactive $CaCO_3$ might be formed at 750°C (1380°F). To explore the matter further, dolomite from Run A22A was cycled at 871°C (1600°F) sulfidation and 760°C (1400°F) regeneration. Run A22A was a continuous run lasting 22 cycles in which the regenerator was run at 760°C (1400°F).

Results of Run A86 are given in Table X-16. The first few cycles gave 80% regeneration, the same as had been observed in the continuous run. However, the $H_2S/CaCO_3$ space velocity at breakthrough was lower than for previous batch runs, and the H_2S in the outlet gas tended to rise as cycling continued. Eventually, the initial H_2S level prior to breakthrough reached the breakthrough concentration so that essentially no sulfidation was carried out. After 13 cycles, the inlet H_2S concentration was reduced from 0.6 to 0.3% and a plateau of 0.08% H_2S was obtained prior to breakthrough. The $H_2S/CaCO_3$ space velocity was only 0.17 at breakthrough in cycle 15.

It is concluded that some of the $CaCO_3$ in the Run A22A material was unreactive thereby giving the low $H_2S/CaCO_3$ space velocity and the high H_2S concentration while excess $CaCO_3$ was still present.

An additional relevant item of information is that examination of a few selected samples of cycled stone using a scanning electron microscope (SEM) equipped for energy dispersive X-ray analysis has disclosed the presence of very large CaS crystals in a matrix of small MgO crystals. These results are detailed in Section XIV. Knowing that large crystals of CaS are formed can aid in explaining the results of Runs A85 and A86.

It is hypothesized that deactivation of CaS is caused by growth of large relatively inert crystals. During normal regeneration, the small CaS crystals are converted to $CaCO_3$ which are reactive by virtue of their size and high surface area. High temperature, long time regeneration converts the interior of the large crystals to $CaCO_3$ by "brute force". These large $CaCO_3$ crystals are fundamentally unreactive. Thus, the $CaCO_3$ fed into Run A85 barely reacted at all. The feed to A86 contained some reactive and some unreactive $CaCO_3$, and therefore performed at a reduced efficiency based on its total $CaCO_3$ content.

Run A128 - Cycling of Half-Calcined Dolomite

Run A128 was a base case run made with fresh half-calcined Canaan dolomite. The products of Runs A87-A95 were combined and then cycled batchwise for four cycles. Figure X-7 shows that results were comparable to those from a continuous run.

TABLE E-14

Conditions and Results for Gas Desulfurization
System Pressure: 15 atm (206 psig)

Run Number	A154	A158
Temperature, °C	927 (1700°F)	871 (1600°F)
Type of Dolomite	Canaan from Run A88	Fresh Canaan
Acceptor Size Consist, Tyler Mesh	28 x 65	28 x 48
Nominal Feed Rate, gm/hr (half-calcined basis)	← Batch →	
Input, SCFH(1)		
Recycle to Bed	80	140
H_2O	12.6	21
H_2	11.9	27
CO	15.6	28
CO_2	4.0	9.3
N_2	158	68
H_2S	← 1 →	
Purges (CO_2) to Bed	← 8 →	
Purges (N_2) above Bed	← 15 →	
Output		
Exit Gas Rate, SCFH (dry basis)	190	142
Composition, Mol %		
H_2	7	17
CO	7	17
CO_2	8	9
N_2	80	56
H_2S	--	--
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	5	9
H_2	7	17
CO	7	17
CO_2	8	9
N_2	75	50
H_2S	--	--
Flow Rate, SCFH, Top of Bed	207	259
Fluidizing Velocity, ft/sec	0.40	0.49

(1) Input is given after shift reaction and hydrolysis of CS_2 have taken place.

TABLE K-15

Conditions and Results for Regenerator
System Pressure: 15 atm (206 psig)

Run Number	A124	A125
Temperature, °C	← 704 (1300°F) →	
Regeneration Time, min.	← 60 →	
Input, SCFH		
Recycle to Bed	← 38 →	
H_2O	← 47 →	
H_2	← 3.0 →	
CO	← 0 →	
CO_2	70	
Purges (CO_2) to Bed	← 10 →	
Purges (N_2) above Bed	← 0 →	
Purges (CO_2) above Bed	← 15 →	
Output		
Exit Gas Rate, SCFH (dry basis)	← 97 →	
Composition, Mol %		
H_2	← 3 →	
CO	← 3 →	
CO_2	← 94 →	
N_2	← 0 →	
H_2S	← -- →	
COS	← -- →	
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	← 30 →	
H_2	← 2 →	
CO	← 2 →	
CO_2	← 66 →	
N_2	← 0 →	
H_2S	← -- →	
COS	← -- →	
Flow Rate, SCFH, Top of Bed	← 166 →	
Fluidizing Velocity, ft/sec	← 0.46 →	

TABLE 2-10

Run [illegible] – [illegible] Cycling of [illegible] Dolomite[a]

Gas Desulfurizer: [illegible]°C ([illegible]°F), Regenerator: [illegible]°C ([illegible]°F)

Gas Desulfurizer:											
Wt. % H₂S, Inlet	Feed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Cycle Number	0	1	2	3	5	7	9	11	13	15	
Wt. %											
CaCO₃	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
CaS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
"CaO"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Wt. % H₂S in Dry Outlet Gas with [illegible] CaCO₃ in Bed		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible] CaCO₃ [illegible] at [illegible] H₂S in Outlet Gas		[illegible]		[illegible]	[illegible]	—	—	—	—	[illegible]	
Regenerator:											
Wt. %											
CaCO₃		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CaS		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
"CaO"		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Percent Regeneration		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

(a) In Run [illegible], [illegible] dolomite underwent [illegible] cycles of sulfidation at [illegible]°C ([illegible]°F) and regeneration at [illegible]°C ([illegible]°F).

E. Cycling with Varying Residence Times

Runs A129-A132

Four batch cycling runs were made employing the possible combinations of 20 or 60 minutes residence time for sulfur absorption and regeneration. Details are presented in Tables X-17 and X-18 and in Figures X-8 and X-9. Tymochtee II dolomite was the feedstock, and each run lasted for 11 cycles. For runs employing 60 minutes in the gas desulfurizer, breakthrough occurred after several cycles. The H_2S feed rate was then reduced from 3 SCFH to 1 SCFH for the remainder of the cycles. In the batch mode of operation, the bed volume continually decreased due to sampling, attrition and handling losses. Data are given for both Runs A129 and A129A. Run A129 was terminated after four cycles due to depletion of the inventory. Thereafter, a larger inventory was used and 11 cycles were achieved in Run A129A.

Most striking was the effect of reducing residence time in the gas desulfurizer. At 10 cycles, going from 60 to 20 minutes in the gas desulfurizer increased regeneration activity from 15 to 40% at 60 minutes regenerator time and from 15 to 43% at 20 minutes regenerator time. Conversely, going from 60 to 20 minutes regenerator time had no effect at the 60 minute desulfurizer level. Another effect observed was that attrition rates were highest at the short gas desulfurizer residence time, 3.3% average for 20 minutes versus 0.8% for 60 minutes.

It is believed that deactivation of stone takes place primarily in the gas desulfurizer due to crystal growth and particle sintering. This would explain the dramatic effect of time on activity. The results of the above runs are highly significant since they indicate the potential for more than doubling the stone's capacity for sulfur absorption. It would be desirable, however, to repeat the runs in a continuous operation.

F. Lab-Scale Batch Acceptor Cycling

Details of the construction of the batch cycler were described in Section IV-F. The unit was set up to allow a small sample to physically be moved from the sulfiding to the regenerating zone of a reactor which maintained dual conditions at all times.

Two runs were made at the conditions shown in Table X-19. Results were based on the weight changes which occur as the acceptor was cycled between the carbonate and sulfide forms. The reactor internals were subject to a high temperature corrosive environment which alternates between mildly oxidizing in the regenerator to highly reducing in the gas desulfurizer. Metal corrosion products and "scale" formed. The "scale" can distort the sample weight if it falls into the holder.

The problem was aggravated by the inability to obtain quick delivery of type 446 stainless steel wire which was needed for the sample support. Type 310 stainless steel wire was used until the middle of Run CR2, when Kanthal A-1 wire was substituted.

FIGURE X-7

Run A12R Deactivation of CaS at 704°C (1300°F)

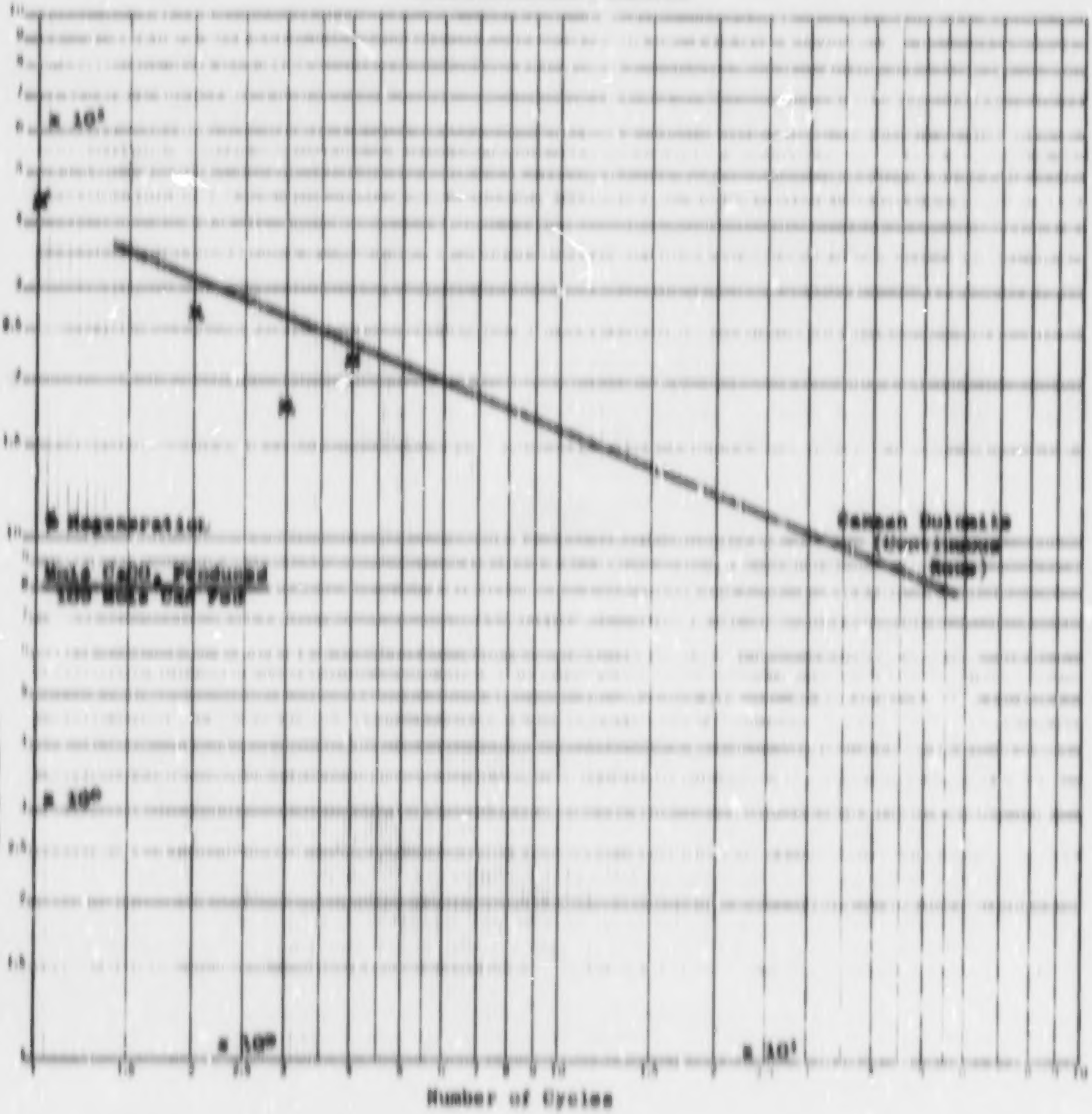


TABLE E-17

Runs A129 to A132 - Conditions and Results for Gas Desulfurizer

System Pressure: 15 atm (206 psig)

Run Number	A129, A130	A131, A132
Temperature, °C	← 871 (1600°F) →	
Type of Dolomite	← Tymochtee 11 →	
Acceptor Size Consist, Tyler Mesh	← 28 x 48 →	
Nominal Feed Rate, gm/hr (half-calcined basis)	← Batch →	
Nominal Run Time, min.	20	60
Input, SCFH(*)		
Recycle to Bed	← 148 →	
H_2O	← 21 →	
H_2	← 27 →	
CO	← 22 →	
CO_2	← 9.3 →	
N_2	← 88 →	
H_2S	← 3.0 →	
Purges (CO_2) to Bed	← 5 →	
Purges (N_2) above Bed	← 15 →	
Output		
Exit Gas Rate, SCFH (dry basis)	← 142 →	
Composition, Mol %		
H_2	← 17 →	
CO	← 17 →	
CO_2	← 9 →	
N_2	← 56 →	
H_2S	← 0.03 →	
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	← 8 →	
H_2	← 17 →	
CO	← 17 →	
CO_2	← 8 →	
N_2	← 50 →	
H_2S	← 0.03 →	
Flow Rate, SCFH, Top of Bed	← 268 →	
Fluidizing Velocity, ft/sec	← 0.43 →	
Attrition, % of Feed	2.7, 1.8	0.07, 0.01

(*) Input is given after shift reaction and hydrolysis of CS_2 have taken place.

TABLE X-18

Runs A128 to A132 - Conditions and Results for Regenerator
System Pressure: 15 atm (206 psig)

Run Number	A128, A129A, A131	A130, A132
Temperature, °C	704 (1300°F)	
Nominal Run Time, min	20	60
Input, SCFH		
Recycle to Bed	55	
H_2O	47	
H_2	5.0	
CO	0	
CO_2	75	
Purges (CO_2) in Bed	10	
Purges (N_2) above Bed	0	
Purges (CO_2) above Bed	15	
Output		
Exit Gas Rate, SCFH (dry basis)	97	
Composition, Mol %		
H_2	3	
CO	3	
CO_2	94	
N_2	0	
H_2S	--	
COS	--	
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	30	
H_2	2	
CO	2	
CO_2	66	
N_2	0	
H_2S	--	
COS	--	
Flow Rate, SCFH, Top of Bed	166	
Fluidizing Velocity, ft/sec	0.48	

FIGURE X-8

Runs A129, A129A - Deactivation of CaO at 704°C (1300°F)

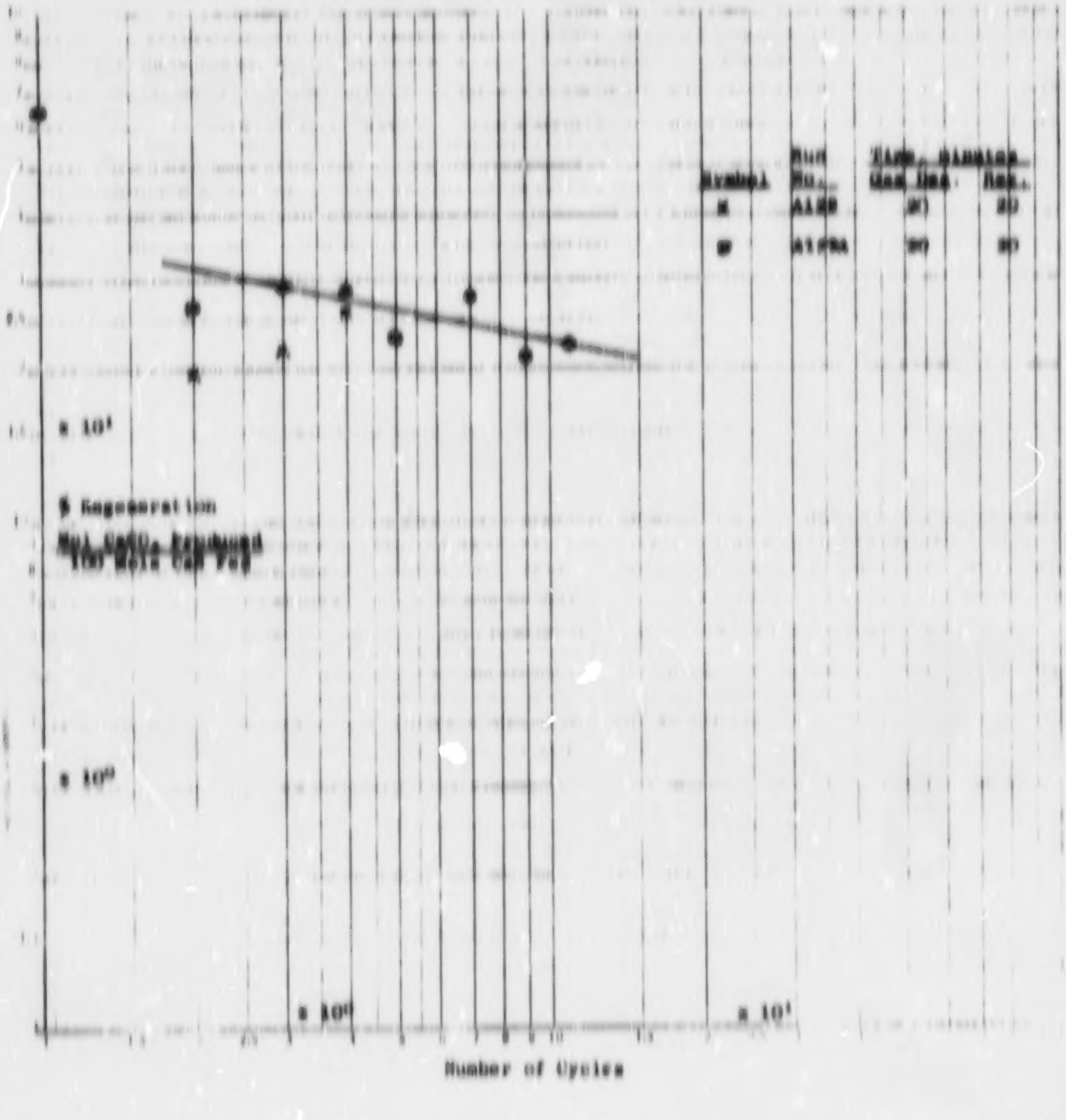
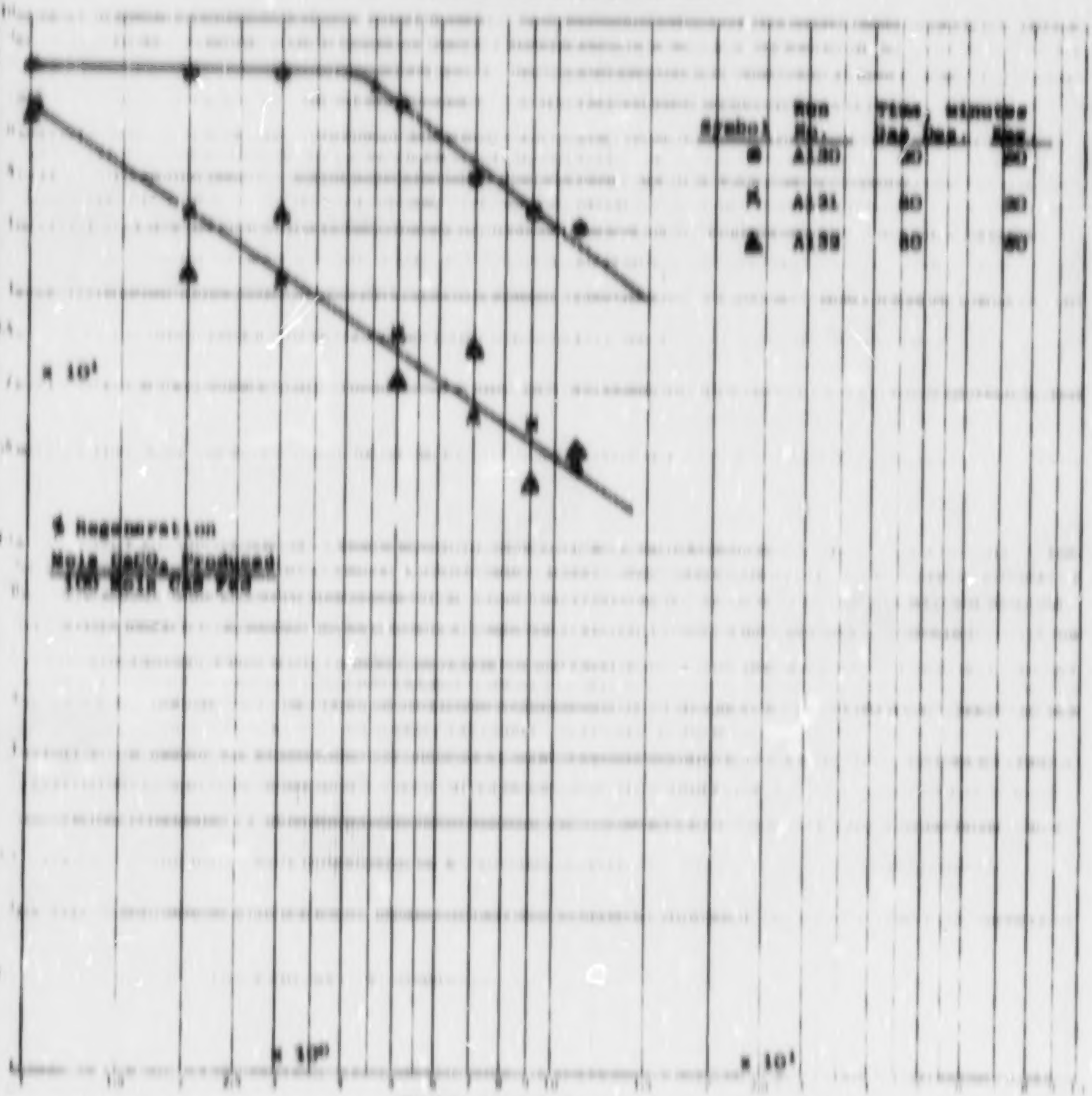


FIGURE X-8

Runs A130 to A132 - Deactivation of CaO at 704°C (1300°F)



Run CR1

In Run CR1 the conversion as judged by the sulfided sample weight loss never reached the equivalent of 88+%. This was apparently due to the presence of scale in the sample. As our experience has been that the acceptor does become completely sulfided, conversions are normalized by the addition of a constant correction factor of 13 mol %, which brought the maximum observed conversion to 99.5% CaS. Data for the 6-1/2 cycles are presented in Table X-20 and Figure X-10. The relative percent regeneration (mols $CaCO_3$ formed per 100 mols of CaS fed) decreased from over 50% in cycle 1 to 10% in cycle 6.

Run CR2

In Run CR2 greater care was exercised to keep scale out of the sample. Some scale inevitably got in, and this was removed magnetically in cycle 9 and after cycle 22. After cycle 22, the sample was removed from the reactor and about one-third of it was missing. The cause of the loss is unknown; the sample may have been jarred or some material might have "popped" out as a result of the chemical cycling.

The sample was cleaned of scale, and then part of it was analyzed for sulfide sulfur content by decomposition in an acidified iodine solution followed by titration with thiosulfate. The regenerated sample, Run 22R, was found to contain 92.9% CaS. Cycle 23S was run, and (by titration) the CaS content had risen to 99.6%. The change corresponded to 6.7%, and the change via the weight loss was about 6.3%. The data are presented in Table X-21 and Figure X-10.

Examination of the data shows that up until scale was removed in cycle 9 calculated conversions to CaS are apparently lower than the true conversion. The CaS form represents a weight loss compared to $CaCO_3$, and it appears that scale in the sample made the weight loss insufficient. When the scale was removed, the weight loss showed a conversion over 100%. Either some dolomite was removed with the scale or had been lost earlier and the loss was offset by scale falling in. While the listing of conversions over 100% is awkward, there is no scientific way to normalize the data, and the raw results have been reported. The last cycle results are believed to be accurate and help to pin down the shape of the deactivation curve shown in Figure X-10.

Batch lab-scale data are compred to data from the continuous unit in Figure X-10. Considering the difficulties encountered in the lab-scale work, the results are in reasonable agreement. Additional development work would be needed before the lab unit could be considered capable of generating precise, accurate data.

The screen analysis of the sample after the run is given in Table X-22. Some slight fines generation (3% -65 mesh) apparently occurred upon cycling even without the rough treatment of a pneumatic lift line or fluidized bed as occurs in the continuous unit.

TABLE 5-10

Conditions for Batch Acceptor Cycling Reactor
Pressure: 15 atm (206 psig)

Charge: 0.4 grams Canaan Dolomite, 20 x 28 Tyler Mesh

Gas Desulfurizer Zone	
Time, minutes	45
Temperature, °C (°F)	871 (1600)
Input, SCFH	
CO_2	1.73
5% H_2S-H_2 Mix	2.10
N_2	6.34
Input After Shift, Mol %	
CO_2	7.5
H_2	10.2
CO	9.65
H_2O	9.65
H_2S	1.0
N_2	62.0
Regenerator Zone	
Time, minutes	45
Temperature, °C (°F)	704 (1300)
Input, SCFH	
CO_2	3.25
H_2O	1.75

TABLE X-20

Results of Lab Scale Cycle Test (R)

Cycle No.	a Change in Conversion, Mol % Ca	b Mol % CaS in Sample	c = b + 13 Mol % CaS in Sample, Normalized	$d = \frac{100\ a}{c}$ Relative Percent Regeneration
1S	49.2	49.2	62.2	--
1R	32.4	16.8	29.8	52
2S	56.0	72.8	85.8	--
2R	46.5	26.3	39.3	54
3S	49.7	75.9	88.9	--
3R	34.4	41.5	54.5	39
4S	38.5	80.0	93.0	--
4R	25.8	54.2	67.2	28
5S	30.5	84.7	97.7	--
5R	17.8	67.0	80.0	18.2
6S	19.5	86.5	99.5	--
6R	17.8	68.7	81.7	17.9
7S	16.7	85.4	98.4	--

FIGURE X-10

Lab-Scale Batch Acceptor Cycling
Sulfidation: 871°C (1600°F)
Regeneration: 704°C (1300°F)

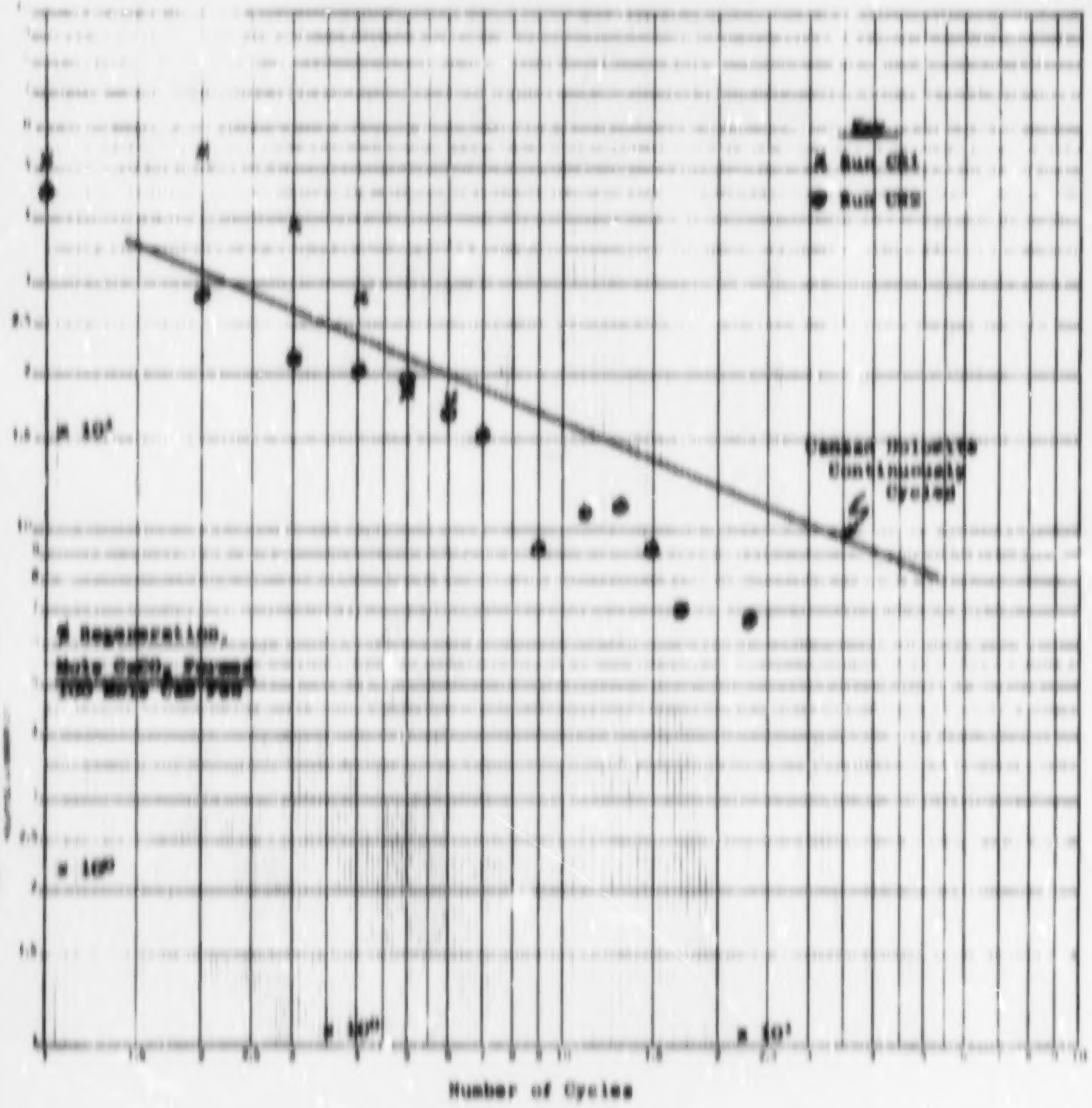


TABLE X-21

Results of Lab Scale Cycle Test CR2

Cycle No.	Change in Conversion, Mol % Ca[1]	Mol % CaS in Sample
1S	76.9	76.9
1R	34.8	42.0
2S	52.2	94.2
2R	28.4	65.8
3S	26.7	92.5
3R	21.4	71.1
4S	21.4	92.5
4R	20.1	72.4
5S	20.3	92.7
5R	19.6	73.1
6S	16.7	89.8
6R	16.7	73.1
7S	15.5	88.6
7R	14.9	73.7
8S	13.1	86.8
Removed Scale		104.1
8R	9.2	94.9
11S	10.8	105.6
11R	10.8	94.8
13S	9.6	104.4
13R	11.1	93.3
16S	13.3	106.6
16R	9.2	97.4
17S	11.6	108.9
17R	7.0	101.9
Removed Scale		
27S	--	99.6[2]
27R	6.7	92.9[2]

(1) In 1R the relative regeneration was 45.3%. For all other cycles, the relative regeneration was assumed equal to the change in conversion.

(2) Based on sulfur analysis of the solids. The change in conversion based on weight difference was 6.3%.

TABLE X-29

Screen Analysis of Run CRS After 33 Cycles

Starting Size: 20 x 28 Mesh

Screen Size, Tyler Mesh	Average Particle Size, Microns	Weight Percent
20 x 28	681	44
28 x 35	503	44
35 x 48	356	7
48 x 65	252	3
-65	208	2

XI. HOT REMOVAL OF PARTICULATES AND ALKALI

Introduction

The low Btu gasification process being developed is intended for application to combined cycle power generation. The gas turbines involved are subject to corrosion by alkali metals volatilized from coal and dolomite and to erosion by particulates. Presently it is proposed to remove particulates and alkali fume at 704°C (1300°F) by means of high pressure drop cyclones. The use of hot filters remains as another viable but less desirable possibility.

It is not known how much alkali will be volatilized from the coal as it goes through the gasification process, but the fraction will certainly be small. There was no significant change in the sodium and potassium contents of Loveridge ash going through devolatilization, a gasification kinetics study and finally the carbon burnup operation.[1] Conoco experience has been that there are no noticeable changes in the alkali content of either ash or dolomite in the Rapid City gasification pilot plant. For Illinois coals, alkali metals are found to be refractory in high and low temperature ashing and "remain entirely in the ash."[15] Fluidized bed boiler studies by Westinghouse[16] assumed that 1% of the coal and dolomite alkali ended up in the gas phase. However, a detailed discussion of the basis for the assumption was not given.

In our process the ratio of coal to makeup dolomite is 50:1, so alkali from dolomite is expected to be of minor importance. Overall removal of > 99.99% of the coal alkali is thought to be required to make the product fuel gas suitable as a gas turbine feed.

The experimental setup was detailed in Section IV. Briefly, the standard gas desulfurizer-regenerator cyclic run was made, and then a programmed amount of alkali-containing material was added to the acceptor fed into the desulfurizer. The gas exit stream was kept hot until after it was filtered on a stainless steel sintered porous plate. The downstream effluent was then analyzed for alkali.

Runs FR1A and FR1B

Ordinarily, the gas desulfurizer is run with a gas feed preheat coil in the upper part of the bed. The preheat coil reduces the temperature of the outlet gas as it heats the inlet stream. This difficulty could not be overcome by adding more heat to the reactor walls as they tended to reach their operating limit. As a compromise measure, the first run, FR1A, was made with a one-half length preheat coil. While the problem of the high wall temperature was eliminated, the temperature in the gas space above the bed was too low 649-704°C (1200-1300°F). The exit line from the reactor to the hot box filters was only 427°C (800°F). Detailed run condition and results are presented in Tables XI-1 to XI-3.

The procedure was to first circulate Canaan dolomite for several sulfiding cycles in order to evaporate any volatile alkali, and to have a bona fide sulfided stone in the bed. When the alkali feed was started, the system was switched to a separate filter and condensate system. After shutdown, the various pipes were rinsed with distilled water and dilute nitric acid to leach any deposited alkali. The condensates and washes were analyzed for alkali via atomic absorption (AA).

TABLE XI-1

Conditions and Results for Gas Desulfurizer
System Pressure: 15 atm (206 psig)

Run Number	FR1A	FR1B	FR2	FR3
Temperatures, °C (°F)				
Bed	← 871 (1600) →			
Space above Bed (Minimum)	660 (1220)	← 760 (1400) →		
Flange	← 621 (1150) →			
Exit Line to Hot Box	427 (800)	← 704 (1300) →		
Hot Box Filter	← 704 (1300) →			
Solids Feeds, gm/hr				
Sulfided Canaan Dolomite, 28 x 48 Tyler Mesh	2000	1930	2050	2080
Raw Tymochtee II Dolomite, -150 Tyler Mesh	26.4	22.5	27.0	(10.2 (Canaan 4
Hillsboro Low Temperature Coal Ash, -150 Tyler Mesh	2.10	3.03	0.0	0.0
NaCl	0.084	0.081	0.43	0.43
Gas Input, SCFH(1)				
Recycle to Bed	95	← 94.5 →		
H_2O	23	← 20 →		
H_2	23	← 26 →		
CO	26	← 22 →		
CO_2	7.1	← 10.0 →		
N_2	0.0	← 0.0 →		
H_2S	2.1	← 2.2 →		
Air	0.0	← 22 →		
Purges (CO_2) to Bed	← 6 →			
Purges (N_2) above Bed	← 16 →			
Purges (N_2) to Bed	← 8 →			
N_2 Lift Gas to Bed	94	← 108 →		
Outlet Gas Top of Bed,(2) Mol %				
H_2O	10	← 11 →		
H_2	16	← 10 →		
CO	16	← 10 →		
CO_2	7.5	← 9 →		
N_2	58	← 60 →		
H_2S	0.09	0.08	0.08	0.08
Flow Rate, SCFH, Top of Bed	202	221	221	221
Fluidizing Velocity, ft/sec	0.42	0.48	0.48	0.48
Duration of Fines Feed, hours	6.5	6.2	4.9	5.9
Removal of Feed + Recycle Sulfur, %	97.4	97.5	97.2	96.9
% H_2S in Outlet/Equilibrium % H_2S	0.9	0.8	0.8	0.9
Conversion of Acceptor/Pass, mol %	15	16	16	16

(1) Input is given after shift reaction and hydrolysis of CH_4 have taken place.
(2) Calculated to fit shift equilibrium.

TABLE XI-2

Conditions and Results for Regenerator
System Pressure: 15 atm (206 psig)

Run Number	FR1A	FR1B	FR2	FR3
Temperature, °C (°F)	704 (1300)			
Nominal Solids Residence Time, min.	50	40	44	50
Input, SCFH				
Recycle to Bed	90			
H_2O	51			
H_2	3.8			
CO	0.0			
CO_2	22			
Purges (CO_2) to Bed	10			
Purges (N_2) above Bed	0.0			
Purges (CO_2) above Bed	15			
Output				
Exit Gas Rate, SCFH (dry basis)	50	45	47	44
Composition, Mol %				
H_2	4.0	4.0	4.4	4.4
CO	6.1	3.5	3.3	3.3
CO_2	88.8	88.7	88.7	89.0
N_2	0	1.3	1.2	1.1
H_2S	2.04	2.08	2.00	2.09
COS	0.1	0.18	0.14	0.17
Outlet Gas, Top of Bed				
Composition, Mol %				
H_2O	28.5	32.0	33.5	31.0
H_2	3.6	3.8	3.3	3.5
CO	4.9	2.7	2.5	2.0
CO_2	61.0	57.8	59.0	59.7
N_2	0.0	1.0	0.9	0.9
H_2S	2.03	2.23	1.58	2.01
COS	0.09	0.14	0.11	0.13
Flow Rate, SCFH, Top of Bed	175	176	181	172
Fluidizing Velocity, ft/sec	0.48	0.49	0.50	0.48
% H_2S in Outlet/Equilibrium % H_2S	0.50	0.61	0.48	0.55
Regeneration of Acceptor/Pass, mol %	8.4	9.5	7.3	8.5

For the first run, NaCl, Tymochtee 11 dolomite fines and low temperature ash were added to the recirculating stream of acceptor. The low temperature ash was made batchwise using the gas desulfurizer vessel at a temperature of 538°C (1000°F) or less. The run was made using sodium chloride doping equivalent to 1% volatilization of alkali in a coal containing 0.17% sodium. Dolomite fines and ash were fed at a rate equivalent to 1% of the feed of these materials to the gas desulfurizer and gasifier, respectively.

Recovery of fines in the hot box filter was poor, and at the same time there was a slight increase in the weight of solids comprising the circulating inventory. It is believed that the proximity of the solids inlet line to the reactor outlet caused some of the fines to be trapped and carried into the regenerator. It is not known how this affected the overall alkali removal efficiency.

Based on the condensate recovery rate observed in Run FR1A, the gas composition corresponded to shift equilibrium of about 704°C (1300°F). It is believed that due to the presence of dolomite and ash fines combined with a modest cool down of gas leaving the reactor rather than the usual quench to about 260°C (500°F), the gas actually did shift down to a lower temperature equilibrium level. The data for gas composition given in Table XI-1 are therefore calculated to give the composition corresponding to shift equilibrium above the bed.

Results for alkali removal are given in Table XI-3. These data taken at face value indicate that alkali removal from fuel gas presents no problem. However, temperatures above the bed and in the exit line were not high enough, and this may have resulted in the deposit of sodium upstream of the filter. Not every connecting line downstream of the filter was rinsed, and something may have deposited on the walls. Glass jars were used for sample storage, and it was later found that several tenths of a ppm of sodium could be leached out of a glass sample container using only distilled water.

The one-half length preheat coil was then removed from the gas desulfurizer, and air was added to the feed gas to provide the needed extra heat. In addition, the exit line was rewound so that it could be brought to a higher temperature. With these changes, Run FR1A was repeated as FR1B. Temperature traverses showed the minimum temperature in the gas space above the bed to be about 760°C (1400°F). The exit line to the hot filter was maintained at 704°C (1300°F). Based on analyses of condensates and washes of process lines, approximately 99.6% of the feed sodium and potassium were removed, and the molar ratio of Na or K in the wet product gas was calculated to be on the order of 5 x 10^{-8}.

Run FR2

It was felt that the ash fed in with the salt in Run FR1B might have reacted with the alkali feeds which would have accounted for the high removal efficiency. Run FR2 was made with a five-fold increase in salt input and no fine ash feed in order to provide a more severe test. The results were about the same. The molar ratio of Na or K in the gas above the bed was estimated to be 2 x 10^{-8}, and the removal efficiency was better than 99%.

Run FR3

Tymochtee dolomite is a relatively impure stone containing clay minerals. As these could react with alkali compounds, a more severe test for alkali removal was to make a run in which Canaan dolomite fines instead of Tymochtee dolomite fines were fed to the unit together with salt. This was done in Run FR3, but again, there was almost no sodium or potassium detected in the effluents downstream of the hot filter. However, whereas the potassium levels in the gas had been 2 x 10^{-6} in Runs FR1A to FR2, the figure for Run FR3 was 13 x 10^{-6}. This may have been due to the lack of Tymochtee dolomite fines in the system. On the other hand, some volatilization of potassium from the Canaan inventory may have occurred which would have added to the totals.

Discussion

It is believed that a lot of the fines were trapped in the desulfurizer bed and carried down to the regenerator. Table XI-3 shows that the -150 mesh material in the beds must be included in order to obtain a reasonable material balance on the fines in the system. The issue is complicated somewhat by the need to make an estimate of the contribution to the fines total made by attrition of the Canaan stone inventory.

The data in Table XI-3 indicate an enrichment of the effluent gas in chlorine relative to sodium. These results are summarized in Table XI-4. The molar feed ratio was about one in all cases while the ratio for the gaseous effluent was 27 for FR1B and about 100 for FR2 and FR3. It is assumed that in the gas desulfurizer chlorine is liberated as HCl which is then washed out in the condensers. The condensates generally displayed a pH of about 3, a rather acid condition. The question remains though, what happens to the sodium half of the NaCl couple? Given below is a reaction which would yield HCl and a potentially nonvolatile sodium compound. It is noted that we have not investigated the associated thermodynamics. Similar reactions can be written for potassium.

$$2\ NaCl + H_2O + 3\ SiO_2 = Na_2O \cdot 3\ SiO_2 + 2\ HCl.$$

The data are not significant quantitatively because of their scatter. However, as far as they go, the data support the contention that the alkali did not escape the hot filter.

Obviously more work is needed. As far as we know, the above experiments were the very first to attempt to come to grips with the question of how much alkali actually would appear in the product fuel gas of a process which employs a hot cleanup technique.

TABLE XI-4

Molar Ratios in Effluent Downstream of Hot Box Filter

Run No.	K/Na	Cl/Na
FR1B	0.47	26.5
FR2	0.91	105
FR3	2.8	78

XII. CHANCE REACTION STUDIES

A. Introduction

The Chance reaction was commercially practiced as early as 1888(17) to remove sulfur from alkali wastes via the reaction,

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S \qquad (XII-1)$$

It is similarly applied to our process in order to remove sulfur from spent CaS so that it may be disposed of without generation of noxious odors. A Chance reactor is now in place at Conoco's Rapid City pilot plant where it is desulfurizing spent dolomite from the CO_2 Acceptor Process which contains a low level of sulfur. The lab study first examined the possibility of using Chance reaction product as a sulfur acceptor to eliminate the requirement for makeup stone, and then went on to survey the rate and efficiency of the reaction for disposal of spent acceptor in order to provide an improved design basis for the commercial use.

B. Discussion

Reactivity of Chance Reaction Products as Sulfur Acceptors

The first few runs were made in order to obtain a bona fide Chance reaction product which could be evaluated for its activity as an H_2S acceptor. It was hoped that a process could be devised whereby spent stone could be reused indefinitely thus obviating the need for fresh make-up stone. The product was prepared by running the Chance reaction in two stages:

$$\text{Hydrosulfidation, } CaS + H_2S = Ca(HS)_{2(aq)}, \qquad (XII-2)$$

$$\text{and Carbonation, } Ca(HS)_{2(aq)} + CO_2 + H_2O = CaCO_3 + 2\,H_2S. \qquad (XII-3)$$

It was then tested in a thermobalance at atmospheric pressure using an H_2S-H_2-CO_2 mix as detailed in Table XII-1.

The thermobalance study showed that even finely divided precipitated $CaCO_3$ was not an active H_2S acceptor. However, the same material after calcining to CaO was active toward H_2S.

The conclusion is, therefore, that the use of the Chance reaction product in an entrained-type dilute phase reactor, is only potentially useful as an H_2S acceptor if the operating temperature is high enough to effect calcination of the $CaCO_3$. Whether the kinetics are suitable for this type of process requires more definitive rate data than were obtained in this study.

Study of Chance Reaction Variables

The next step in the program was a rapid survey of the principal variables controlling the rate of reaction. A detailed kinetic correlation of the data was not attempted. CO_2 reacts not only with CaS or $Ca(HS)_2$ but also with MgO according to the reaction,

TABLE III-1

Conditions and Results for Sulfidation of Chance Reaction Products

Run No.	Feed Material	Hydrosulfiding Temperature, °C (°F)	Carbonation Temperature, °C (°F)	Product Surface Area, m^2/g	Time for 90% Reaction of Product with H_2S,[1] minutes: $CaCO_3$ Form at 900°C	Time for 90% Reaction of Product with H_2S,[1] minutes: CaO Form at 980°C	Remarks
C31	Fisher CaO	Ambient	Ambient	4.1	[2]	65	
C32	Fisher CaS, as received	—	60 (140)	N.D.	[2]	N.D.	100% Recovery of $CaCO_3$ from CaS
C33	Run 87 Gas Desulfurizer Sample, 10 cycles, -200 mesh	90 (194)	90 (194)	27.4	[2]	N.D.	
C34	Fisher CaS, as received	60 (140)	88 (190)	4.8	[2]	40	100% Recovery of $CaCO_3$ from CaS
—	Fresh Tymochtee Dolomite, 20 x 35 mesh	—	—	—	62	30	

[1] Composition of treating gas: 0.65 vol. % H_2S, 12.75 vol. % H_2 and 86.35 vol. % CO_2.
[2] The initial progress of the reaction indicated that conversion would stop before 90% was achieved.

$$MgO_{(s)} + CO_{2(g)} + H_2O_{(l)} = Mg(HCO_3)_{2(aq)}, \qquad \text{(XII-4)}$$

at low temperature, and the reaction,

$$MgO_{(s)} + CO_{2(g)} + H_2O_{(l)} = MgCO_{3(s)}, \qquad \text{(XII-5)}$$

above 40-50°C. The mechanism of the Chance reaction itself is uncertain with respect to whether it is mainly a single-step reaction,

$$CaS_{(s)} + H_2O_{(l)} + CO_{2(g)} = CaCO_{3(s)} + H_2S_{(g)}, \qquad \text{(XII-1)}$$

or a two-step reaction,

$$CaS_{(s)} + H_2S_{(g)} = Ca(HS)_{2(aq)}, \qquad \text{(XII-2)}$$

$$Ca(HS)_{2(aq)} + CO_2 + H_2O = CaCO_3 + 2\ H_2S. \qquad \text{(XII-3)}$$

The time and equipment available were insufficient to provide a complete study of the system, but show at least the directional effects of the major variables.

At the beginning, the sulfur content of the final dry product and the H_2S content of the exit gas as a function of time were determined. In later runs, the sulfur content of the slurry as a function of time was also followed. The data are summarized in Tables XII-2 and XII-3. It is noted that the gas compositions in Table XII-3 represent averaged values since it took about ten minutes to produce a 90% step change in composition at the flow rates employed. Also, the slurry sampling procedure introduced a variation in the weight of solids found in a given slurry sample. Three samples of the same slurry gave 5.34%, 5.88% and 5.18% solids at an actual composition of 5.88 wt % solids. The slurry analysis gave both sulfide sulfur in the solid and H_2S, HS^- and $S^=$ dissolved in the liquid.

The parameters explored in the study were temperature, feedstock, particle size, CO_2 flow rate and stirrer speed. The solids:liquid weight ratio and stirrer speed had little impact on the interfacial area (judged visually) over the range studied. The data in Tables XII-2 and XII-3 are inconclusive as to the precise effect of stirrer speed, but it is clear that any effect is relatively minor.

Runs CH5 through CH7A studied the effect of temperature. In going from 21°C to 88°C, the rate increased dramatically, i.e., the residual sulfur in the product dropped from 24% to 0.35%. Because of this result, it was decided to investigate only the higher temperature of 88°C (190°F).

Reaction rate was also dramatically increased by decrease in particle size as can be seen by comparing Run CH11 with Run CH13. Going from 20 x 35 mesh to -200 mesh reduced the sulfur content of dry product from 1.27% to 0.16%. A similar trend was observed in going from 28 x 35 mesh to 35 x 65 mesh in Runs CH18A through CH22.

The choice of feedstock also affected the reaction. The Run A6 product did not desulfurize as easily as Run A15 material. However, the A6 material had been cycled through both the CO_2 Acceptor Process regime and the sulfur cycle, so it may not have represented a material which had seen only the sulfur cycle.

[illegible]

[illegible]

[illegible]
[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		—	—						[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		—	—						[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	—	—					[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		—	—						[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		—	—						[illegible]	[illegible]	[illegible]
[illegible]			[illegible]	[illegible]			[illegible]			[illegible]	[illegible]	
[illegible]			[illegible]				[illegible]			[illegible]	[illegible]	
[illegible]		[illegible]	[illegible]				[illegible]		[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]		*			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]		—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		
[illegible]			—	—	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	
[illegible]			—	—		[illegible]			[illegible]	[illegible]	[illegible]	
[illegible]			—	—		[illegible]			[illegible]	[illegible]	[illegible]	
[illegible]			—	—		[illegible]			[illegible]	[illegible]	[illegible]	
[illegible]		[illegible]	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]			—	—	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	
[illegible]			—	—	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	

* [illegible]

[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

Prior treatment by a hydrosulfiding step, i.e., by reaction (XII-2) was helpful in treating such a refractory feedstock as can be seen by comparing Runs CH10, CH11 and CH12, respectively. Run CH10 did not involve hydrosulfiding prior to treatment with CO_2 while in CH11 and CH12, the slurry was first treated with H_2S for 60 and 120 minutes, respectively. Run CH12 showed the lowest residual sulfur content of all three products in that series.

Run CH14 was made to simulate a possible gas environment of sulfided acceptor going through a countercurrent Chance reactor system. It first would see a very high H_2S concentration, and at the exit it would see a very high CO_2 concentration. The sulfur content of the dry solids was reduced to 0.26% from 20% even though a reduced level of CO_2 equivalent to only 1.25 times the estimated stoichiometric amount was used. However, the soluble material left in the liquid was higher than in any other run. This was attributed to $Ca(HS)_2$ which may not have seen sufficient CO_2 to be converted to $CaCO_3$. The soluble material is usually assumed to be $Mg(HCO_3)_2$ formed from $MgCO_3$ and residual CO_2 as the reactor is cooled.

During slurry conversion by CO_2, the appearance of the solid acceptor changed from individual grains into fine particles. After filtration, the solids had a fluffy appearance and occupied several times the bulk volume of the feed. As the run progressed, the viscosity of the slurry increased (visually judged). This change in viscosity could influence the CO_2-slurry interface and diffusion of CO_2 in the aqueous part of the slurry. Settling characteristics of converted slurry were good.

C. Conclusions

It was shown that, on a dry basis, 95+% sulfided spent acceptor containing 20% sulfur can be converted to a 0.03% sulfur form for disposal. The reaction can be run at atmospheric pressure at about 80°C with a residence time of one hour.

TABLE XII-3

Claus Reaction: Composition of Slurry and Exit Gas

Run Number		Time, Min. → 0	12	24	36	48	60	72	84
C5	Gas*	—	2.77	0.56	0.25	0.16	0.16	—	—
C6	Gas	—	1.40	1.05	0.80	0.72	0.67	—	—
C7A	Gas	—	29.0	39.0	30.0	17.0	1.16	—	—
C8A	Gas	—	0.50	0.27	0.22	0.22	0.23	—	—
C9	Gas	—	0.39	0.25	0.25	0.21	0.29	—	—
C10	Gas	—	0.50	0.48	0.38	0.35	0.35	—	—
C16A	Gas	—	25.2	47.0	38.0	17.1	0.09	—	—
	Slurry**	1.57	1.29	.863	.317	.070	.014	—	—
C17	Gas	—	18.1	18.1	19.7	0.34	0.08	—	—
	Slurry	1.57	.938	.525	.0943	.0227	.0066	—	—
C18	Gas	—	35.5	30.0	21.4	0.50	0.14	—	—
	Slurry	1.57	1.01	.386	.0579	.0096	.0060	—	—
C19A	Gas	—	38.0	4.34	0.13	0.05	0.04	—	—
	Slurry	1.57	.361	.106	.0085	.0061	.0038	—	—
C20	Gas	—	22.2	18.4	1.14	0.00	0.08	—	—
	Slurry	1.57	.989	.222	.0494	.0083	.0035	—	—
C21	Gas	—	23.2	28.0	30.8	16.2	2.12	0.11	0.08
	Slurry	1.53	1.88	.847	.342	.0751	.0214	.0027	—
C22	Gas	—	19.0	16.6	4.21	0.09	0.05	—	—
	Slurry	1.53	1.27	.477	.108	.0083	.0053	—	—
C23	Gas	—	19.6	14.2	0.41	0.39	0.31	0.27	0.23
	Slurry	1.53	1.13	.339	.226	.224	.185	.157	.147

* Volume % of H_2S in exit gas; balance CO_2.

** Grams of sulfur/100 grams of slurry.

XIII. PROCESS IMPROVEMENT STUDIES

A. Introduction

Process improvement studies were concentrated in two areas. The first involved the use of a sorbent other than half-calcined dolomite. This was to enlarge the number of suitable sorbents, to lessen the cost of makeup, or to increase the range of the desulfurizer operating conditions. The other area of study was to produce a liquid-phase Claus reactor feed without resorting to burning sulfur and then recovering SO_2 in an absorption tower.

B. Use of Fine Calcined Limestone

An alternate process concept for hot desulfurization of producer gas would use very finely divided CaO. Product CaS would then be regenerated with water and CO_2 at low temperature via the Chance reaction. The advantages of such a process are: The required make-up rate of fresh acceptor would be drastically reduced since wet regeneration of CaS can be carried out to completion, and the gasifier can be run hotter and more efficiently as the gas desulfurizer is operated at calcining conditions.

Attempts to test the concept by using a slurry of precipitated chalk were plagued with difficulties in feeding the slurried solids. Two runs were then made feeding finely ground Nebraska limestone into an expanded bed of coarse solids.

As shown in Figure IV-5, the gas desulfurizer was equipped with a feed line to the bottom of the vessel through which the fine limestone was fed. The reacted stone was elutriated from the coarse bed and collected in the empty regenerator vessel which was equipped with filters to effect gas-solids separation. The run temperature was 927°C (1700°F) and the collection vessel was held at 315°C (600°F).

Run conditions for the two runs are given in Table XIII-1, and assays on the product fines are given in Tables XIII-2 and XIII-3. For Run L1, the bed material was 28 x 35 mesh deadburned dolomite. Sufficient limestone was fed to give 80-90% conversion of solids. Approximately 93% of the feed sulfur was removed, but analysis of the bed material showed that the deadburned dolomite had participated in the reaction. About 10% of the CaO in the deadburned dolomite was converted to CaS. The elutriated product had been 58% converted to CaS.

In Run L2, the coarse bed material was 35 x 48 mesh fused MgO which is totally unreactive toward H_2S at run conditions. Only 78% of the feed sulfur was reacted, and the exit H_2S concentration was 0.28%. The product stone was 58% converted to CaS. Shutdown of the run was conducted so as to immobilize the bed in order to determine the fines content. Based on the fines content, the fines residence time was estimated to have been 1.6 minutes.

Table XIII-3 gives the solids compositions as a function of particle size. It is noted that in both runs there was a period in which the stone was fed without H_2S in the vessel. This was approximately 15% of the acceptor in Run L1 and 8% in Run L2. In all cases, there was $CaCO_3$ present, and the $CaCO_3$ content generally increased with decreasing particle size. The CaS content

TABLE XIII-1

Conditions and Results for Fine $CaCO_3$ Runs
Pressure: 15 atm (206 psig)

Run Number	L1	L2
Temperature, °C	927 (1700°F)	941 (1725°F)
Bed Material	Dead Burned Dolomite	Magnorite
Size Consist, Tyler Mesh	28 x 35	35 x 48
Feed Material	← Nebraska Limestone →	
Size Consist, Tyler Mesh	65 x 150	150 x 200
Feed Rate, gm/hr, Raw Stone	270	227
Input, SCFH(1)		
Recycle to Bed	261	232
H_2O	21.4	51.5
H_2	25.0	41.8
CO	33.0	54.0
CO_2	8.8	11.0
N_2	71.0	85.0
H_2S	1.8	3.0
Purges (CO_2) to Bed	5.0	5.0
Purges (N_2) above Bed	10.0	10.0
Purges (CO_2) above Bed	10.0	10.0
N_2 Lift Gas to Bed	65.0	65.0
Output		
Exit Gas Rate, SCFH (dry basis)	214	286
Composition, Mol %		
H_2	9.0	16.5
CO	13.9	21.0
CO_2	8.8	11.4
N_2	68.3	50.8
H_2S	0.06	0.28
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	5.9	10.2
H_2	8.5	15.5
CO	13.6	19.7
CO_2	8.6	8.7
N_2	65.0	45.7
H_2S	0.06	0.26
Flow Rate, SCFH, Top of Bed	305	351
Fluidizing Velocity, ft/sec	0.76	0.79
Removal of Feed Sulfur, %	93.9	76.0
Removal of Feed Plus Recycle Sulfur, %	85.1	68.4
% H_2S in Outlet/Equilibrium % H_2S	5.2	19.0
Conversion of Acceptor, Mol %	77	66
Estimated Acceptor Residence Time, min.	(a)	1.6

(1) Input is given after shift reaction and hydrolysis of COS have taken place.
(a) Not available.

generally increased with decreasing particle size. The data are too meager to do more than speculate on the mechanism which gave the above results.

It is concluded that although significant reaction of fine $CaCO_3$ (CaO) took place, sufficient reactivity to prevent H_2S breakthrough remains to be demonstrated.

C. Generation of an Active Acceptor from Coarse Limestone

Two attempts were made to obtain active $CaCO_3$ in a porous matrix starting with limestone. In Run A40, 35 x 48 mesh Rapid City limestone was calcined at 927°C (1700°F) in nitrogen and then recarbonated at 760°C (1400°F) in CO_2. The recarbonated stone was fed to the gas desulfurizer at 871°C (1600°F) with the standard gas flows. While the bed was being fed in and sulfided, temperature aberrations were observed and the run was stopped. Upon disassembly of the reactor, a large agglomerate was found at the bottom of the vessel.

In Run A41, the stone was simultaneously calcined and sulfided at 927°C (1700°F) in nitrogen and CS_2. The product was 80% CaS, with some residual $CaCO_3$ and "CaO". This product was then fed through the regenerator and put into the unit for cyclic operation. Results are detailed in Tables XIII-4 and XIII-5 and in Figure XIII-1. Pickup of H_2S proceeded without breakthrough until the $CaCO_3$ content of the stone was depleted. This occurred with 3-5% $CaCO_3$ remaining in the stone leaving the gas desulfurizer. Attrition was only 0.3%. Regeneration was poor having dropped to ca. 3% by cycle 3.

Run A49

For Run A49, a limestone feed was to be cyclically sulfided in the calcined state at 927°C (1700°F) followed by standard regeneration at 704°C (1300°F). Rapid City limestone (Minnekhata) was the feed for this run. However, in the presence of sulfur, agglomeration with attendant defluidization was a continuing problem.

Sulfidation was first attempted in a cyclic operation using the gas composition and temperature shown in Table XIII-4. However, fluidization could not be maintained, and inspection of the bed after shutdown showed it to be agglomerated. A feedstock of sulfided limestone was then prepared batchwise. The bed was fed in and calcined using only nitrogen and CO_2 as the fluidizing medium. Sulfidation was then carried out as shown in Table XIII-4. The sulfidation was run at about 9% per hour with satisfactory desulfurization of the inlet gas until breakthrough at ca. 40 mol % CaS in the stone. The beds contained about 0.3% of +20 mesh agglomerates.

Five batches were combined for cyclic operation. However, attempts to run in this mode were unsuccessful because agglomerates continually choked the transfer line between vessels. The run was abandoned at this point. The attrition rate was qualitatively judged to be 1% or less for the brief period when sulfided stone was being fed to the unit.

D. Fully Calcined Dolomite

Runs A120-A122, A125-A127

Six batch runs were made at 927°C (1700°F) under fully calcined conditions. Detailed run conditions and results are presented in Tables XIII-4 and XIII-6. Table XIII-4 shows somewhat different conditions for A120-A122 and

TABLE XIII-2

Particle Size Analysis of Product Limestone Fines

Material		L1 Product -65 Mesh	L1 Bed -65 Mesh	L2 Product -150 Mesh	L2 Bed -150 Mesh
Percent	65 x 100	16.8	84.8	--	--
Size	100 x 150	35.8	13.7	--	--
Consist,	150 x 200	30.3	1.0	80.5	75.6
Tyler	200 x 325	5.0	0.3	18.0	17.1
Mesh	-325	8.8	0.1	1.5	7.3

TABLE XIII-3

Analysis of Product Limestone Fines

Material	Size Consist, Tyler Mesh	Mol %		
		$CaSO_4$	CaS	CaO
L1 Product, -65 Mesh	65 x 100	5.9	72.3	21.9
	100 x 150	11.0	66.8	22.2
	150 x 200	20.9	54.7	24.4
	200 x 325	31.2	41.4	27.4
	-325	34.8	33.8	31.4
	whole -65 sample	13.9	57.8	28.4
L1 Bed, -65 Mesh	65 x 100	2.1	86.4	11.5
	100 x 150	3.0	82.9	14.1
	150 x 200	11.3	62.9	25.8
	200 x 325	13.1	55.0	31.9
L2 Product, -150 Mesh	150 x 200	18.7	59.4	21.9
	200 x 325	19.6	59.5	20.9
	-325	21.1	45.8	33.1
	whole -150 sample	17.9	59.0	23.1
L2 Bed, -150 Mesh	150 x 200	54.8	30.3	14.9
	200 x 325	32.3	42.7	25.0
	-325	5.9	15.4	78.7

FIGURE XIII-1

RUN A41 - DEACTIVATION OF CaS AT 704°C (1300°F)

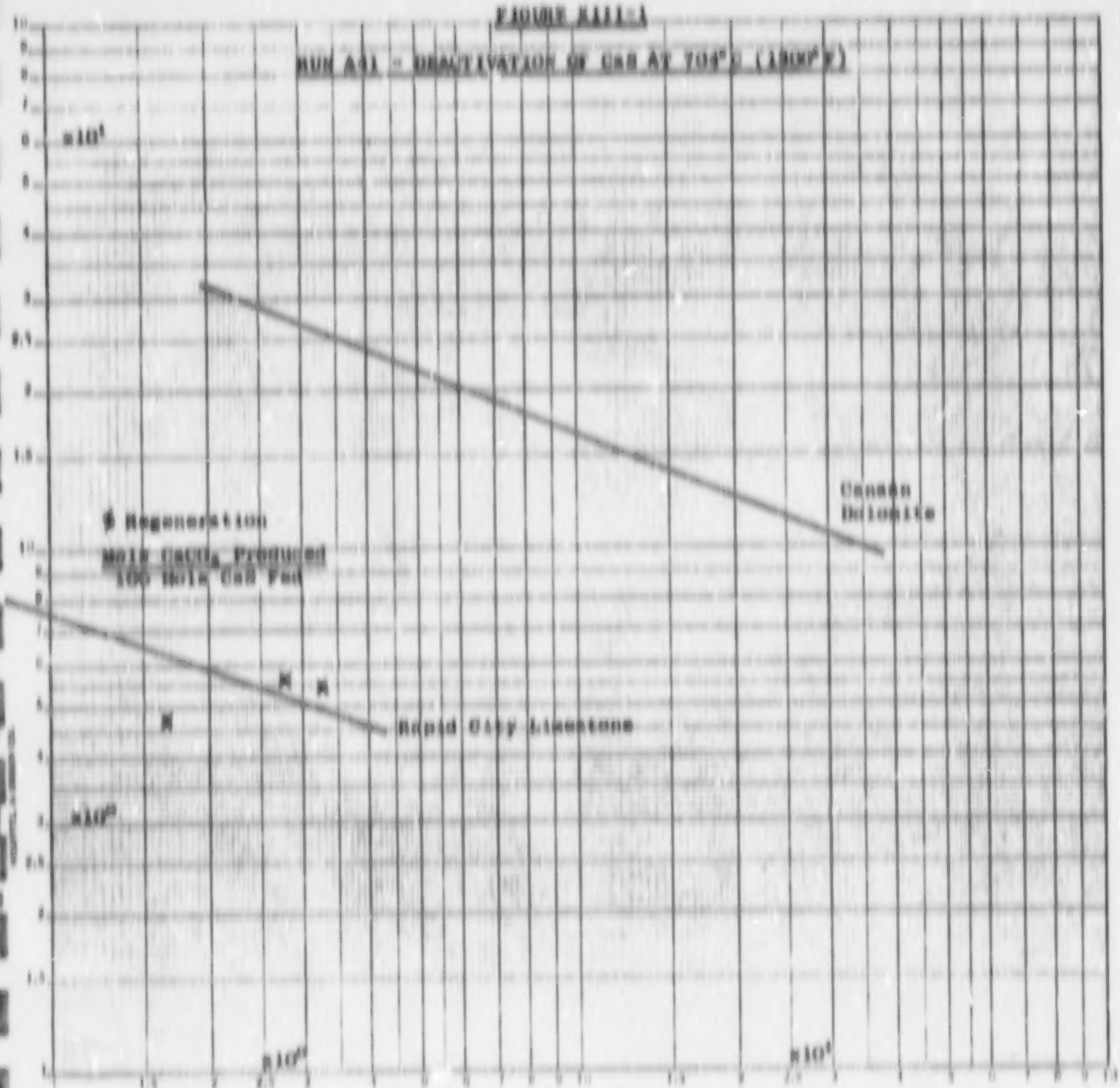


TABLE [illegible]

Conditions and Results for Gas Desulfurization
System Pressure: [illegible] atm ([illegible] psig)

Run Number	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Temperature, °C (°F)	[illegible] ([illegible])	[illegible] ([illegible])	[illegible] ([illegible])		
Type of [illegible]	[illegible]		[illegible]		
Acceptor Size Consist, Tyler Mesh	[illegible]		[illegible]		
Nominal Feed Rate, gm/hr (calcined basis)	[illegible]	Batch	Batch		
Nominal Solids Residence Time, min.	[illegible]	[illegible]	—	—	—
Input, SCFH[1]:					
Recycle to Bed					
H_2S	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H_2O	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Purges (CO_2) to Bed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Purges (N_2) above Bed	0	[illegible]	[illegible]	[illegible]	[illegible]
Purges N_2 to Bed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Recycle Acceptor Lift Gas, above Bed	[illegible]	0	0	0	0
Outlet to Stack	[illegible]	0	0	0	0
Exit Gas Rate, SCFH (dry basis)	[illegible]	[illegible]	—	—	—
Composition, mol %	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H_2S	[illegible][2]	[illegible]	—	—	—
Outlet Gas, Top of Bed					
Composition, mol %					
H_2O	9.2	[illegible]	[illegible]	[illegible]	[illegible]
H_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H_2S	[illegible]	[illegible]	—	—	—
Flow Rate, SCFH, Top of Bed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Fluidizing Velocity, ft/sec	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Attrition, % of Feed Rate	[illegible]	[illegible]			
Duration of Circulation with H_2S Feed, hr	[illegible]	Batch			
Removal of Feed Sulfur, %	[illegible]	[illegible]			
Removal of Feed Plus Recycle Sulfur, %	[illegible]	[illegible]			
% H_2S in Outlet/Equilibrium, % H_2S	[illegible]	[illegible]			
Conversion of Acceptor/Pass, mol %	[illegible]	[illegible]			

[1] Input is given after shift reaction and hydrolysis of [illegible] have taken place.
[2] Gas sample taken after breakthrough had occurred.

TABLE AIII-8

Conditions and Results for Regenerator
System Pressure: 15 atm (200 psig)

Run Number	A41	A122
Temperature, °C (°F)	←— 704 (1300) —→	
Nominal Solids Residence Time, min.	43	60
Input, SCFH		
Recycle to Bed	0	38
H_2O	55	47
H_2	6.0	5.0
CO	0	0
CO_2	84	70
Purges (CO_2) to Bed	10	10
Purges (N_2) above Bed	5	0
Purges (CO_2) above Bed	10	15
Output in Cycle	3	--
Exit Gas Rate, SCFH (dry basis)	130	97
Composition, Mol %		
H_2	3.40	2
CO	1.17	3
CO_2	83.3	94
N_2	11.3	0
H_2S	0.74	--
COS	0.03	--
Outlet Gas, Top of Bed		
Composition, Mol %		
H_2O	31.0	30
H_2	2.70	3
CO	0.91	3
CO_2	58.9	68
N_2	5.9	0
H_2S	0.57	--
COS	0.02	--
Flow Rate, SCFH, Top of Bed	170	166
Fluidizing Velocity, ft/sec	0.49	0.37
% H_2S in Outlet/Equilibrium % H_2S	0.16	--
Regeneration of Acceptor/Pass, mol %	4.9	--

TABLE [illegible]

[illegible]

Pressure: [illegible] Temperature: [illegible]

Run No.	Conc., [illegible]	Type of [illegible]	Bed Height, [illegible]	Superficial [illegible] Time, sec	Length of Run, min	% of [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Space Velocity at Breakthrough [illegible]	[illegible]		[illegible]		
												[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	.40	Column 3	14.2	2.3	480	3.4	.03	.01	3.4	6.9	1.37	2.09	238.7	1.4	89.4	9.2
[illegible]	.39		9.4	2.2	452	12.4	.01	0	0.2	10.0	1.39	2.13	232.0	6.2	85.5	8.3
[illegible]	.38		4.1	0.9	280	31.1	.02	0	2.9	8.9	3.47	2.09	139.4	3.9	88.1	8.0
[illegible]	.33		4.2	0.8	180	35.9	--	.01	7.8	13.3	4.30	2.08	257.7	7.8	87.0	5.2
[illegible]	.40		20.4	1.9	220	32.7	.03	0	2.3	3.6	7.20	2.06	239.4	3.8	88.3	7.7
[illegible]	.43		23.9	2.9	281	17.8	.03	0	0.3	1.7	[illegible]	2.09	237.1	0.3	90.9	8.8

A125-A127. A stuck rotameter float caused the hydrogen flow in Runs A120-A122 to be low. Due to shift equilibrium, this caused the CO_2 level to be too high, for which the operator compensated by reducing the CO_2 flow as well in order to maintain a calcining condition.

The outlet H_2S concentration was at equilibrium, and the H_2S:CaO space velocity at breakthrough was consistent with data reported for half-calcined stone. However, considerable scatter in the space velocity results was observed.

When the stone was assayed, $CaCO_3$ was found to be present. It is assumed that recarbonation took place as the material was drained through the CO_2-purged exit line.

Run A123

The products of Runs A120-A122 were combined and then cycled batchwise in the fully calcined regime. Run conditions for the gas desulfurizer and regenerator are given in Tables XIII-4 and XIII-5, respectively. Residence time in the desulfurizer varied as the stone was cycled and is, therefore, not given under the conditions cited in Table XIII-4. Results of cycling are presented in Table XIII-6 and in Figure XIII-2. High utilization of the CaO was obtained but, as shown in Figure XIII-2, regeneration was poorer than had been observed in continuous runs with half-calcined stone. It is believed that the long hold time together with the elevated temperature in the gas desulfurizer in cycle 1 may have contributed to the poor regeneration results.

A continuing problem with CaO based acceptors has been agglomeration. At the end of the second sulfidation, weak agglomerates were observed. No difficulties due to agglomerates were experienced in any other cycle.

It is concluded that it may be possible to run the gas desulfurizer under calcining conditions. Potential problems are agglomeration and consumption of CO_2 in the regenerator upon reaction with unconverted CaO.

E. Reaction of $CaSO_4$ with H_2S to Produce Liquid Claus Feed

Introduction

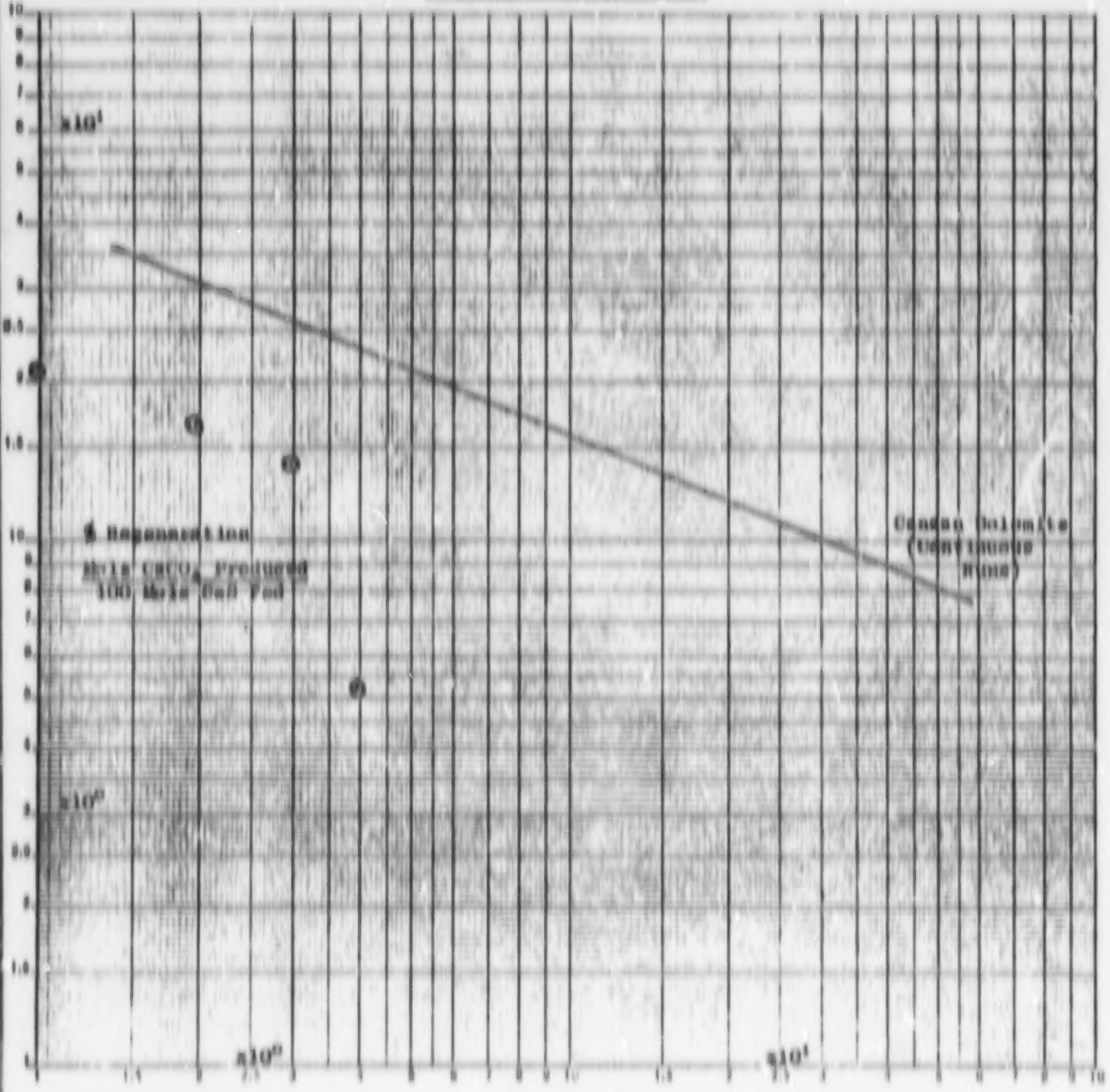
In reference (1) a process was proposed in which the regenerator offgas reacts with $CaSO_4$ to produce directly a liquid-phase Claus feed containing the required 2:1 ratio of H_2S/SO_2. A simplified flow diagram of the process is shown in Figure XIII-3. Potential advantages are that the sulfur combustor, SO_2 absorption tower, liquor circulation piping, and liquid-liquid heat exchangers, all shown in Figure III-3, would be eliminated.

In the process, CaS in the spent acceptor is oxidized with air to form $CaSO_4$ which reacts with the regenerator offgas at about 1600°F. After reaction, the acceptor is processed through the Chance reactor before being discarded. The principal reaction is,

$$3/4\ CaSO_4 + H_2S = 3/4\ CaS + SO_2 + H_2O \qquad (XIII-1)$$

FIGURE XIII-2

RUN A155 DEACTIVATION OF
CaO AT 704°C (1300°F)



Routine operation of the regenerator has shown that other reactions also occur which produce small amounts of elemental sulfur, COS, CO, and H_2. A brief experimental program was done to test the feasibility of the process.

Experimental

A batch of Tymochtee dolomite was sulfated using the same techniques described in Section IX. In a preliminary experiment (Run AB3, not otherwise discussed here) large amounts of elemental sulfur formed which plugged the piping downstream of the reactor. Before plugging occurred the dry product gas showed no detectable SO_2 content ($\leq$ 0.01 mol %). This fact strongly indicated that most of the elemental sulfur was formed in the presence of liquid water condensate by the liquid-phase Claus reaction:

$$2\ H_2S + SO_2 = 3\ S + 2\ H_2O \qquad \text{(XIII-2)}$$

The equipment then was modified to the configuration shown in Figure IV-12 by adding a heated catch pot to retain some of the condensate and nearly all of the elemental sulfur.

Run AB4

The first two parts of Run AB4 were made with a fluidized bed of inert fused periclase (MgO) in order to help distinguish the separate effects of the gas phase reactions and of reaction (XIII-1).

The third and fourth parts of the run were made with sulfated Tymochtee dolomite as bed material. Two temperatures, 860 and 893°C (1580 and 1640°F), were used with each bed material.

The input gas to all parts of the run was a mixture of steam and dry recycle product gas, along with added CO_2 and CH_4. Recycle gas was used to simulate conditions in an upper portion of the bed in a tall commercial reactor.

Run conditions and results are given in Table XIII-7. Assay results for the feed and product acceptor are shown in Table XIII-8. The acceptor was not assayed between Runs AB4C and AB4D. However, the acceptor weight loss was the same in both parts of the run. Therefore, the contributions to or from the acceptor shown in Table XIII-7 were apportioned equally to each run, using the data in Table XIII-8. Since $CaCO_3$ was present, the reaction,

$$CaCO_3 + H_2S = CaS + CO_2 + H_2O$$

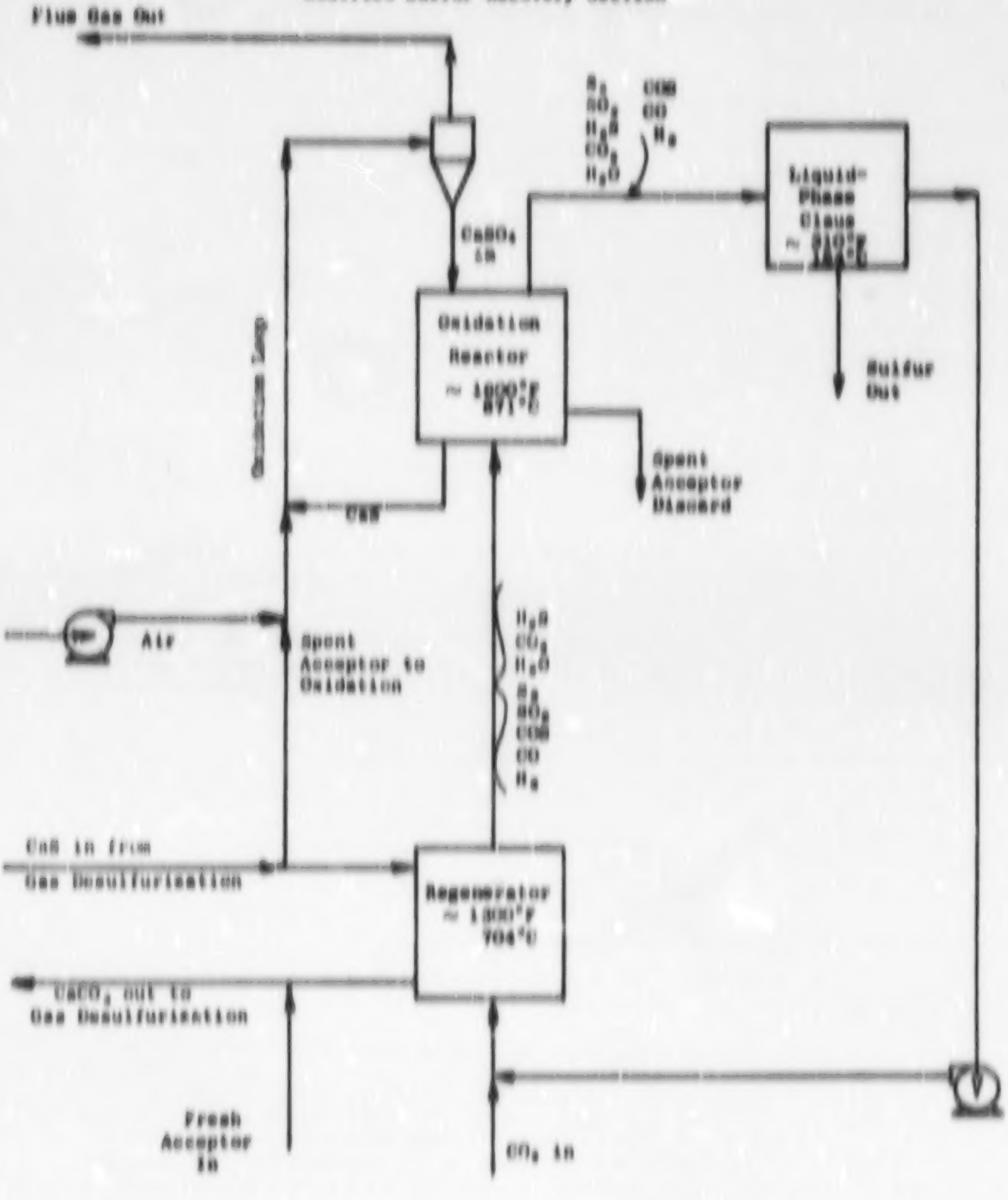
also occurred in addition to reaction (XIII-1).

In all parts of the run, small amounts of COS, CO, and H_2 were found in the dry product gas, as expected.

Since the compositions of the product gases were altered by the reactive environment downstream of the reactor, direct assessment of the conversion of H_2S to SO_2 in the fluidized beds is not possible. Based on experience gained during development of the CO_2 Acceptor Gasification Process, we have found that gas phase reactions involving sulfur species, as well as reactions of CaS and $CaSO_4$, are very rapid at temperatures above about 649°C (1200°F), especially when catalyzed by coal ash and impurities in the acceptor.

FIGURE XIII-2

Modified Sulfur Recovery Section



Flue Gas Out
S_2
SO_2
H_2S
CO_2
H_2O
COS
CO
H_2
Liquid-Phase Claus
~ [illegible]
$CaSO_4$ in
Oxidation Reactor
~ 1600°F
871°C
Oxidation Loop
Sulfur Out
Spent Acceptor Discard
CaS
Air
Spent Acceptor to Oxidation
H_2S
CO_2
H_2O
S_2
SO_2
COS
CO
H_2
CaS in from Gas Desulfurization
Regenerator
~ 1300°F
704°C
$CaCO_3$ out to Gas Desulfurization
Fresh Acceptor In
CO_2 in

TABLE XIII-7

Conditions and Results for Reaction of $CaSO_4$ with H_2S
System Pressure: 15 Atm (205 psig)

Run No.	AB4A	AB4B	AB4C	AB4D
Temperature, °C	860 (1580°F)	893 (1640°F)	860 (1580°F)	893 (1640°F)
Bed Solids	Fused Periclase, Inert		Sulfated Tymochtee II	
Size Consist, Tyler Mesh	← 48 x 65 →		← 35 x 48 →	
Duration of Run minutes	407	58	240	240
Input, SCFH				
Recycle Gas	140	140	128	128
H_2O	135	135	124	124
CO_2	← 18 →			
CS_2	.72	.80	1.00	1.15
Purges to Bed (CO_2)	← 5 →			
Purges above Bed (CO_2)	← 5 →			
Input by Component, SCFH(1)				
H_2O	133.6	133.4	122.0	121.7
CO_2	155.2	154.2	149.6	150.1
CO	1.70	2.38	.90	.93
H_2	1.80	1.88	1.04	1.05
H_2S	5.92	6.38	3.15	3.08
COS	.44	.58	.31	.31
Contribution from/to Acceptor, grams/hr				
Oxygen from Acceptor	0	0	34.8	34.8
Carbon from Acceptor	0	0	.07	.07
Sulfur to Acceptor	0	0	2.60	2.60
Output(2)				
Exit Gas Rate, SCFH (Dry Basis)	29.7	30.0	33.9	33.8
Composition, Mol %				
CO_2 (by diff.)(3)	93.88	93.11	97.35	97.65
CO	1.26	1.69	.70	.73
H_2	1.35	1.40	.81	.82
H_2S	3.20	3.40	.90	.56
COS	.31	.40	.24	.24
Flow Rate, Top of Bed, SCFH	299.2	299.1	278.9	277.3
Fluidizing Velocity, ft/sec	.43	.45	.40	.42

(1) After hydrolysis of CS_2 via $CS_2 + 2\ H_2O = 2\ H_2S + CO_2$.
(2) The actual recovered gas (after condensation of elemental sulfur and water), which escaped the reactive environment downstream of the reactor.
(3) Taken by difference for consistency in subsequent calculations. Actual measured values were, respectively, 94.6, 93.0, 97.5, and 98.0%.

TABLE XIII-8

Acceptor Compositions for Runs A84C and A84D

	Feed in Run A84C		Product from Run A84D	
	Wt %	Grams	Wt %	Grams
CaS	3.16	78.7	18.13	403.6
$CaSO_4$	58.58	1459.3	41.97	934.3
$CaCO_3$	7.24	180.3	5.19	115.5
Inerts, including MgO	31.02	772.6	34.71	772.6
	100.00	2491	100.00	2226*
Distribution of Calcium, Mol %				
CaS		8.0		41.1
$CaSO_4$		78.8		50.4
$CaCO_3$		13.2		8.5

* Obtained by forced calcium balance. Some of the product acceptor was spilled. Actual recovered weight was 2086 grams. Operator estimated 100 grams spillage.

Equilibrium calculations therefore provide accurate estimates of the gas compositions at the top of the bed in Run A84. The exit gas compositions corresponding to equilibria in the following reactions were calculated.

$$\begin{aligned} CO + 1/2\ S_2 &= COS \\ H_2 + 1/2\ S_2 &= H_2S \\ 2\ H_2 + SO_2 &= 1/2\ S_2 + 2\ H_2O \\ CO + H_2O &= CO_2 + H_2 \end{aligned}$$

Results are shown in Table XIII-9. Although some conversion of H_2S to SO_2 occurred in the inert beds, transfer of oxygen via reaction (XIII-1) provides a closer approach to the desired goal of a 2:1 ratio of H_2S/SO_2.

The nature of the downstream reactions can be inferred by comparison of the dry gas compositions taken from Table XIII-9 with the measured compositions of the recovered dry gas. Inspection of the gas compositions, termed Conditions I and III, in Table XIII-10 show that the dry, top-of-bed gases all contain more CO and H_2S, less COS, and about the same amount of H_2 than do the actual product gases. If the assumption is made that all of the incremental COS in the product gas is formed by an overall reaction which occurs at nonequilibrium conditions in the downstream environment and which can be expressed as,

$$3\ CO + SO_2 = COS + 2\ CO_2 \qquad \text{(XIII-3)}$$

and if all the remaining SO_2 reacts in the heated catch pot via reaction (XIII-2), then the dry gas compositions shown as Condition II in Table XIII-10 are obtained. Very good agreement between Conditions II and III was obtained in all four cases. Other combinations of possible reaction paths such as formation of thionic acids (e.g., $H_2S + 3\ SO_2 = H_2S_4O_6$) or the reactions:

$$\begin{aligned} 3\ H_2 + SO_2 &= H_2S + 2\ H_2O \\ 2\ COS + SO_2 &= 3\ S + 2\ CO_2 \end{aligned}$$

gave poor concordance in all cases.

E. Conclusions

Little success was obtained in attempts to use raw limestone as an H_2S sorbent. Calcined limestone was a good sorbent, but regeneration was poor. It may be possible to use calcined dolomite as a sorbent as rates of desulfurization and regeneration appear to be satisfactory. However, there may be some difficulties due to agglomeration.

The process for reacting the regenerator offgas with $CaSO_4$ to produce a liquid-phase Claus feed having the required 2:1 ratio of H_2S/SO_2 was shown to be chemically feasible.

TABLE XIII-9

Calculated Gas Compositions, Run AR4

Run No.	AR4A	AR4B	AR4C	AR4D
Temperature, °C (°F)	860 (1580)	893 (1640)	860 (1580)	893 (1640)
Gas Composition, Top of Bed, Mol %				
H_2O	44.70	44.58	44.30	44.18
CO_2	51.87	51.18	53.58	53.58
CO	.844	1.204	.578	.717
H_2	.894	.804	.403	.48[illegible]
H_2S	1.864	1.888	.889	.790
COS	.081	.085	.040	.036
SO_2	.119	.100	.077	.336
N_2	.031	.044	.030	.121
	100.005	99.994	100.004	100.008
H_2S/SO_2	15.7	18.4	8.14	2.36

TABLE [illegible]

Comparison of Dry Gas Compositions,* Run [illegible]

Run Number	[illegible]			[illegible]			[illegible]			[illegible]		
Temperature, °C (°F)	[illegible]			[illegible]			[illegible]			[illegible]		
Condition	I	II	III	I	II	III	I	II	III	I	II	III
Gas Composition, Vol %												
CO_2	93.30	93.50	93.60	92.36	93.20	93.11	96.12	97.50	97.45	95.87	97.64	97.45
CO	1.71	1.23	1.26	2.17	1.50	1.69	1.03	.54	.70	1.29	.87	.73
H_2	1.28	1.36	1.25	1.45	1.46	1.40	.72	.73	.81	.81	.82	.82
H_2S	3.37	3.27	3.20	3.35	3.45	3.40	1.56	.91	.90	1.36	.50	.56
COS	.15	.30	.31	.17	.40	.40	.57	.26	.14	.17	.26	.26
SO_2	.25	0	0	.29	0	0	.50	0	0	.40	0	0

* After condensation of elemental sulfur and water.

I – Equilibrium dry gas composition at top of bed (data from Table [illegible]).
II – Calculated dry gas composition after completion of downstream reactions (see text).
III – Actual measured composition of final product gas.

XIV. PHYSICAL EXAMINATION OF PRODUCT SOLIDS

A. Surface Area and Pore Volume Data

Pore volume and surface area data are presented in Table XIV-1. Most of the surface areas reported were in the range of 2-3 M^2/g. It appears that surface area decreases slightly as the stone is cycled, but the changes are insignificant compared to the changes observed in regeneration activity. Similarly, pore volume up to 5000 angstroms was in the range of 0.10 to 0.18 cc/g, but porosity changes occurring as a result of cycling are small compared to the change observed in activity. The data in Table XIV-1 go up to 10,000 angstroms for pore volume. The data in this range show a slight increase in pore volume with cycling, however, it is considered that pores of this size may include microcracks as well as actual pores.

B. Sulfur Distribution in Sulfided Dolomites

Figures XIV-1 to XIV-7 show the unspecific electron microprobe images and sulfur, magnesium, and calcium X-ray images of particles present in the sulfided dolomite. The particles were mounted in Bakelite and polished so that cross sections of the particles are shown. When more than one particle was imaged, an A was added to the sample number.

At low conversions, the samples varied in sulfur penetration. Figure XIV-1 shows a prerun sulfided particle for which the sulfur is present in a shell on the outside. Figure XIV-2 shows a particle from the same sample which displays deep sulfur penetration which left three small areas nearly sulfur free. Figures XIV-3 and XIV-4 present oxidized particles from the hardening procedure. In both stones, the sulfur is concentrated on the outside, but is present throughout. Figures XIV-5 and XIV-6 are from a sample which had experienced about one cycle in the process. The sulfur is present throughout the stone, but in Figure XIV-6 an area of high magnesium content can be seen which is relatively free of sulfur. The cycled stone presented in Figure XIV-7 shows a uniform distribution of sulfur along the entire cross section.

In another study a number of acceptor samples were mounted in resin, sectioned, and examined under low power magnification illuminated by short wave ultra violet (UV) light. Calcium sulfide fluoresces under short wave UV light and the distribution of sulfur in the solid can be visually observed. At low conversions and few cycles, an outer shell of CaS was observed in sulfided samples from Runs A27, A32, A33 and A33A. The list includes a 20 x 28 mesh Canaan dolomite sample, and 20 x 28 and 35 x 48 mesh Tymochtee dolomite samples. A series of cycled Canaan dolomite samples regenerated at 593°C, 704°C and 760°C (1100, 1300, 1400°F) showed the 593°C sample to fluoresce at a qualitatively different shade than the others.

The results indicate that, at low conversions, the sulfur may be distributed in a shell on the outside of the particle. This would be consistent with a mechanism of either shrinking core diffusion or kinetic control of the reaction. However, it is also clear that cracks in the particles can allow sulfur to penetrate the interior of particles even at low conversions. At high conversion, or after several cycles, sulfur is uniformly distributed in

Preceding page blank

the particles. In addition, examination of cycled samples from the regenerator do not show any preferential distribution of the residual inert CaS in the stone.

The above considerations lead one to the conclusion that it might be possible to ascribe a shrinking core reaction model to the stone on its first or second cycle. However, this does not follow for subsequent cycles. The presence of natural imperfections in the stone may further complicate the reaction mechanism. It is suggested that in a bed containing particles with a distribution of ages, the kinetics may well be too complicated to handle with a rigorous kinetic calculation. However, a simplified model which assumes the reaction to occur uniformly in the particles could conceivably lead to a usable kinetic correlation for the desulfurization reaction.

C. Scanning Electron Microscope Examinations

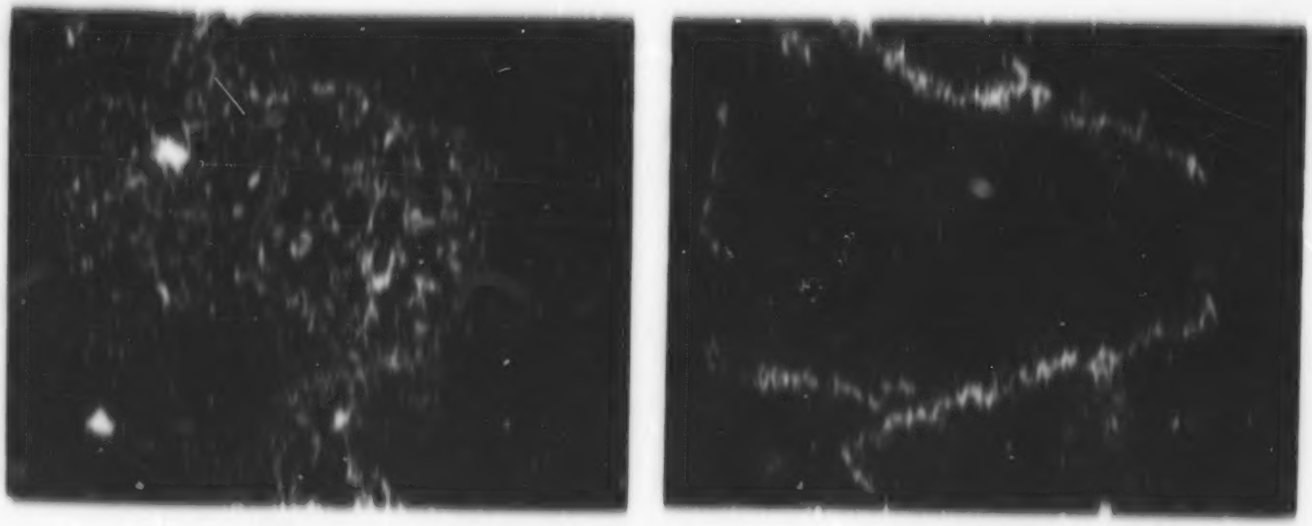
Two series of scanning electron microscope (SEM) pictures of dolomite samples were obtained. The pictures were combined with energy dispersive X-ray analysis to determine the elemental nature of the materials being observed. Figure XIV-8 shows A70 product, a sulfided cycled stone. The picture shows the the presence of small MgO crystals together with large crystals of CaS. Figure XIV-9 shows A81 feed and A81 product. The feed was cycled dolomite which had been regenerated for 8 hours at 704°C (1300°F). The product was regenerated for an additional 8 hours at 871°C (1600°F) and contained very little residual CaS. The feed material shows the presence of large CaS crystals and small crystals of Ca and Mg without sulfur, i.e., MgO and $CaCO_3$. The product shows no evidence of sulfur in the crystals which were examined. The large crystals which formerly contained CaS had been desulfurized to $CaCO_3$.

The next series of photos was obtained by the Illinois State Geological Survey. The sample analyzed was the gas desulfurizer bed of Run A46. This was a highly sulfided stone which had undergone 48 cycles. Individual grains could not be identified, and only the relative elemental mol ratios over an area of the photo are given. A further difficulty in evaluating the photo was induced by the uncertainty of the depth to which the analytical X-ray beam penetrated. Figure XIV-10 gives a view of the exterior surface. Large and small grains can be seen. It appears that there is somewhat more sulfur associated with the larger grains. Figure XIV-11A is a view of the fine grained area on the outer surface, and a lower sulfur content is indicated. In Figure XIV-11B, a view of large grains from a fracture surface on the particle interior shows a higher sulfur level. Figure XIV-12 represents an entirely different phenomenon. Rather large crystals of a sulfur-free material high in Mg, Ca and Si are observed. It is believed that these are magnesium-calcium silicates which are formed when the dolomitic structure reacts with silica impurities in the stone. There is insufficient data to confirm whether these are immediately formed upon calcining, or whether they continue to grow as the stone is cycled.

The key piece of information relevant to a deactivation model is that the CaS is present as very large crystallites in the cycled stone. It is assumed that as the stone is cycled, the calcium species grow and the CaS form does not regenerate readily. The photo of the regenerated material which was the A81 feed shows large grains of CaS which apparently could not be regenerated along with small grains of $CaCO_3$ which were regenerated. Under the brute force conditions of an 871°C (1600°F) regeneration even the refractory CaS was converted to $CaCO_3$ as indicated by Figure XIV-[illegible]. The model which relates deactivation to crystal growth will be elaborated upon in Section XV which discusses variable effects in the system.

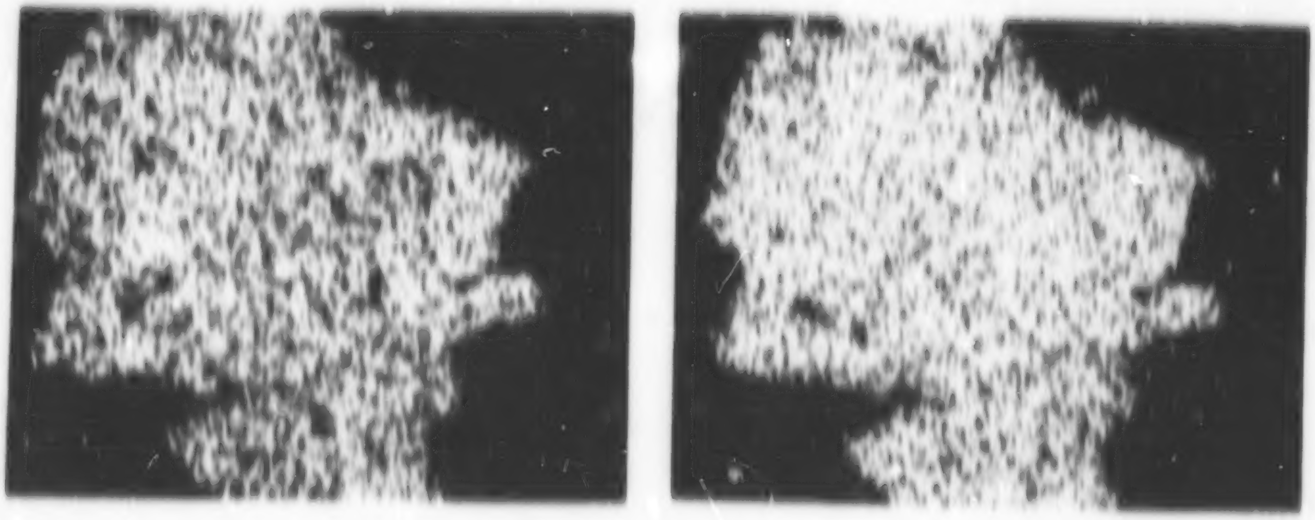
Runs A97, A98, and A107 - Preparation of Samples

If it could be determined in which reactor crystal growth actually takes place, it might be possible to change conditions to retard such growth and thereby prolong sorbent life. Toward this end beds of dolomite were held at reactor conditions for 16 hours while samples were taken for future analysis. Runs A97 and A107 were at gas desulfurizer conditions of 871 and 899°C (1600 and 1650°F), respectively. Run A98 was at regenerator conditions at 704°C (1300°F). These samples remain in storage as reference materials, and no measurements have been made on them to date.



Unspecific image,
reversed sample current

S X-ray

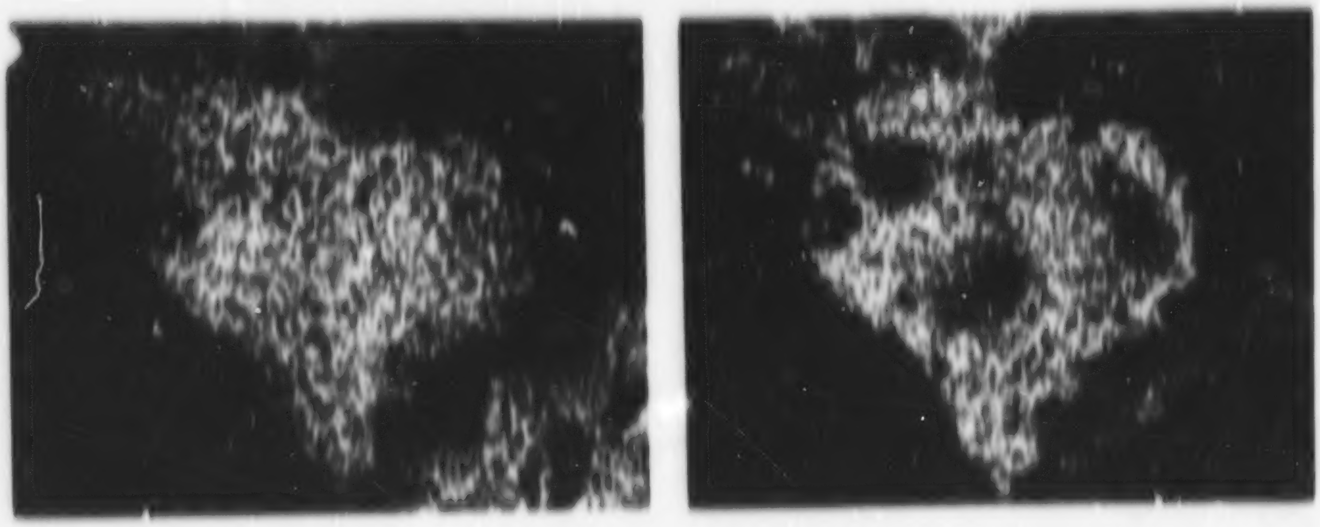


Mg X-ray

Ca X-ray

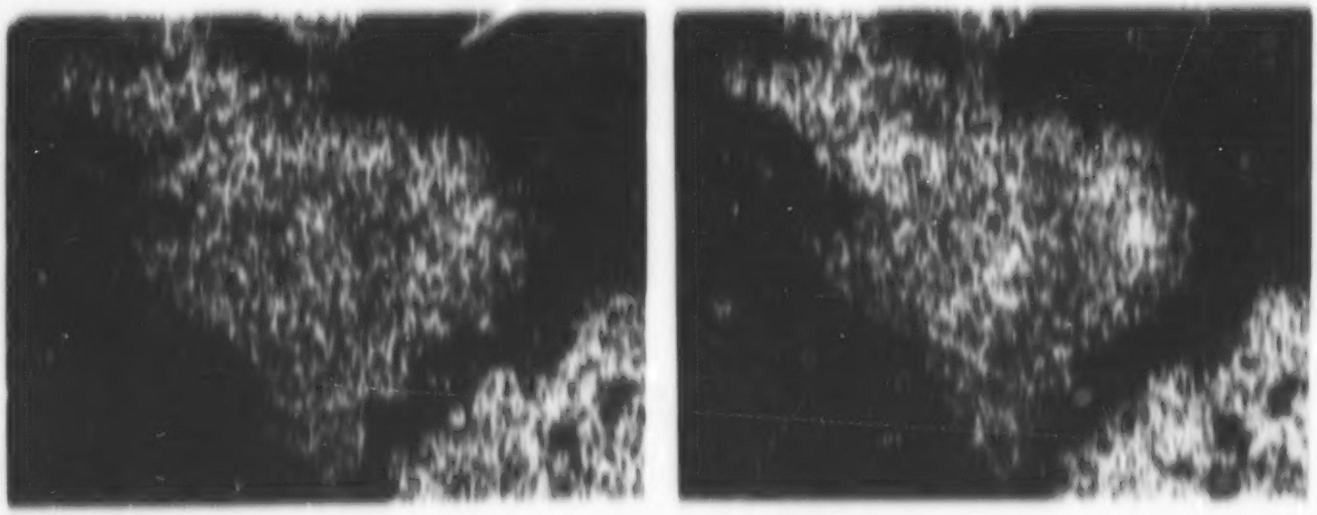
FIGURE XIV-1

Images of Sample A41-1 at 180X. Prerun sulfided to 15 mol % CaS.



Unspecific image,
reversed sample current

S X-ray

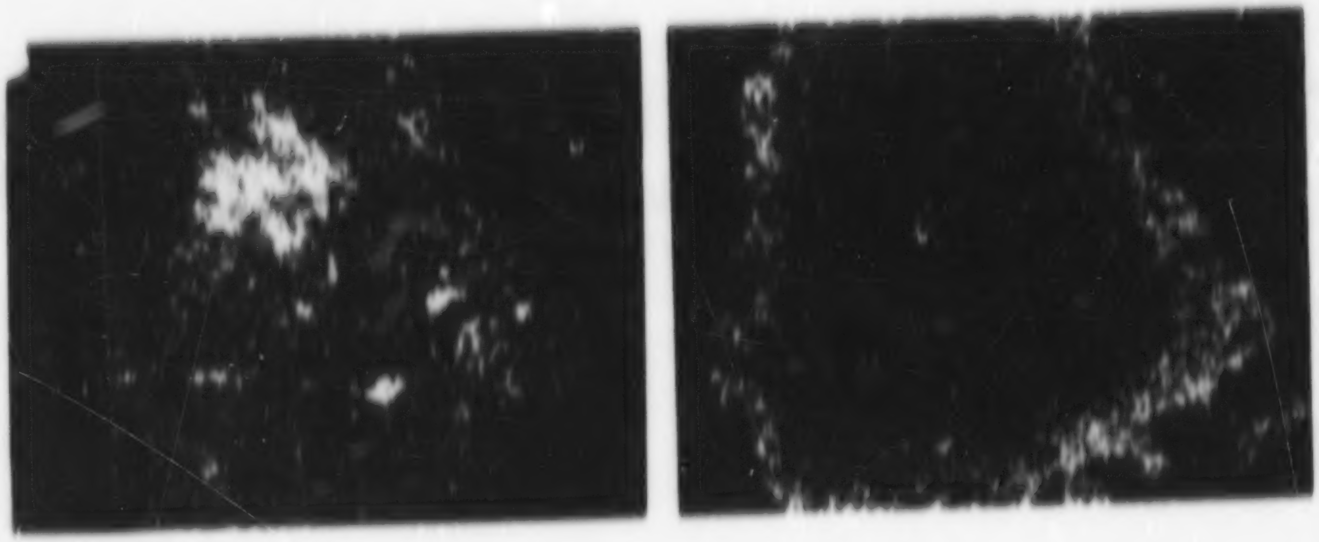


Mg X-ray

Ca X-ray

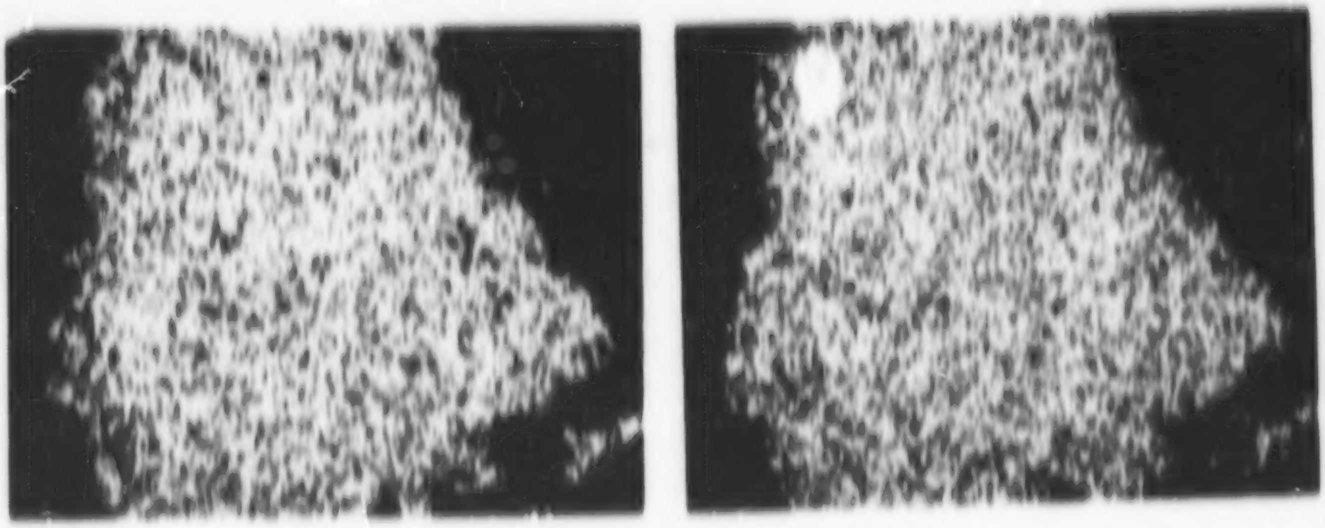
FIGURE XIV-8

Images of Sample A42-1A at 200X. Proton sulfided to 15 mol % CaS.



Unspecific image,
reversed sample current

S X-ray

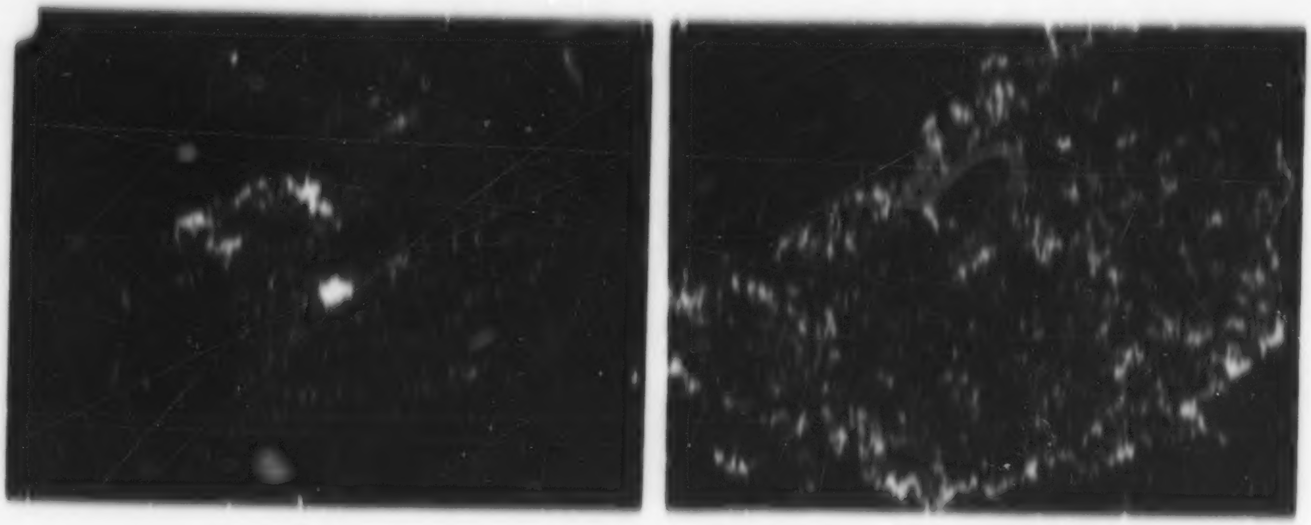


Mg X-ray

Ca X-ray

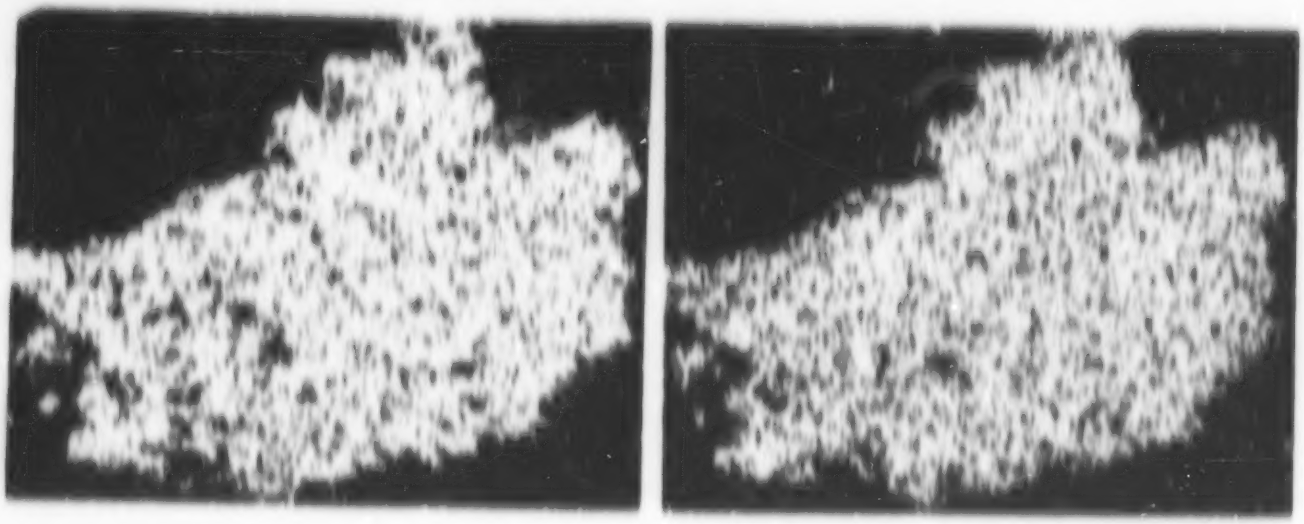
FIGURE XIV-3

Images of Sample A42-2 at 180X. Prerun oxidized to 14 mol % $CaSO_4$.



Unspecific image,
reversed sample current

S X-ray

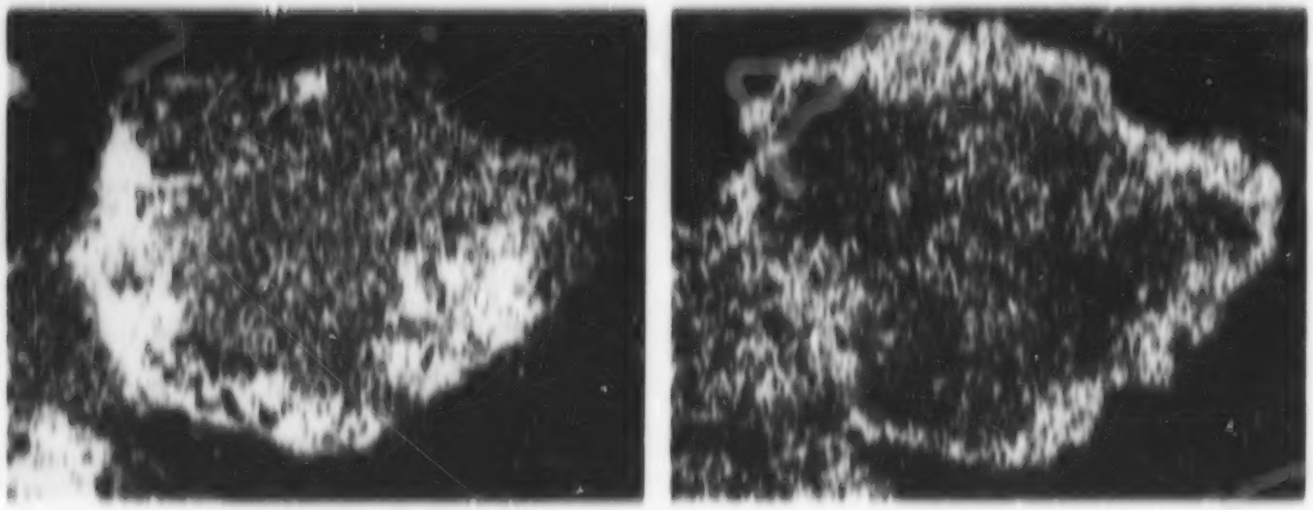


Mg X-ray

Ca X-ray

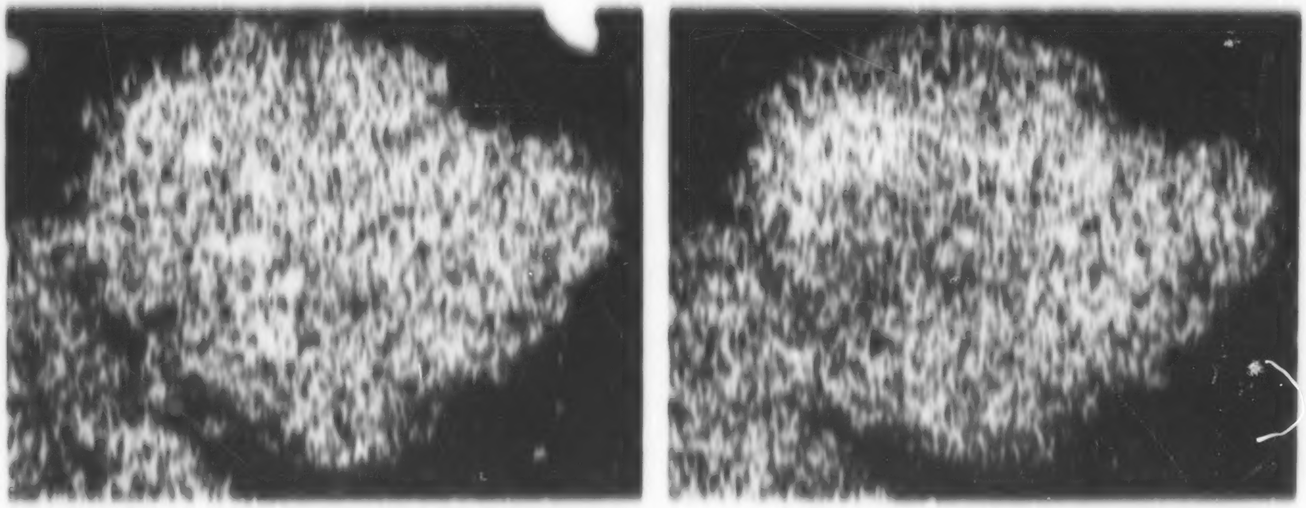
FIGURE XIV-4

Images of Sample A42-2A at 150X. Prerun oxidized to 14 mol % $CaSO_4$.



Unspecific image,
reversed sample current

S X-ray

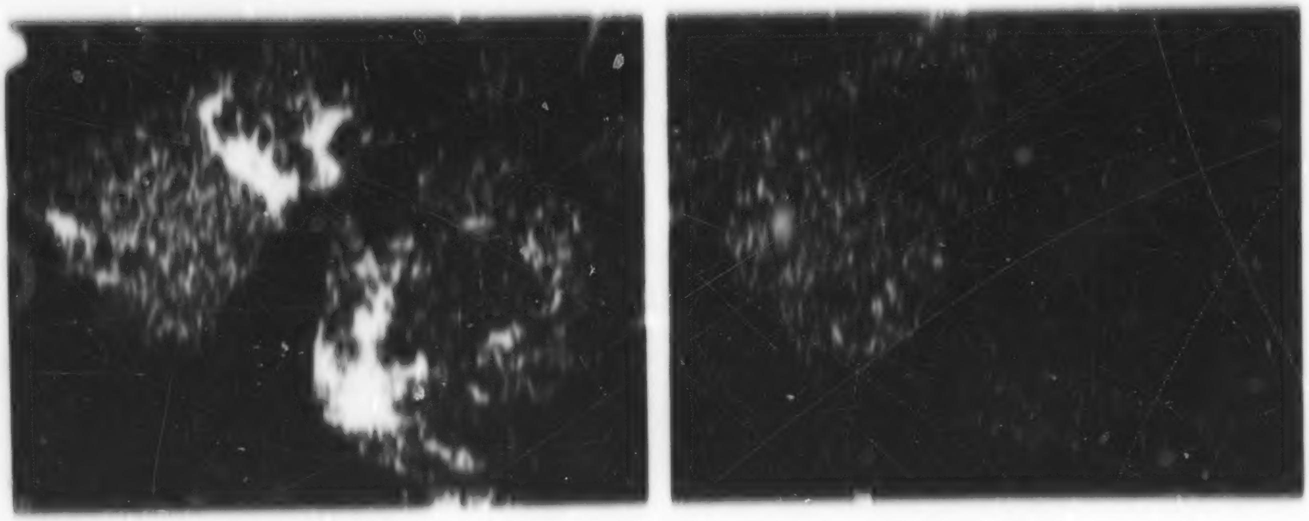


Mg X-ray

Ca X-ray

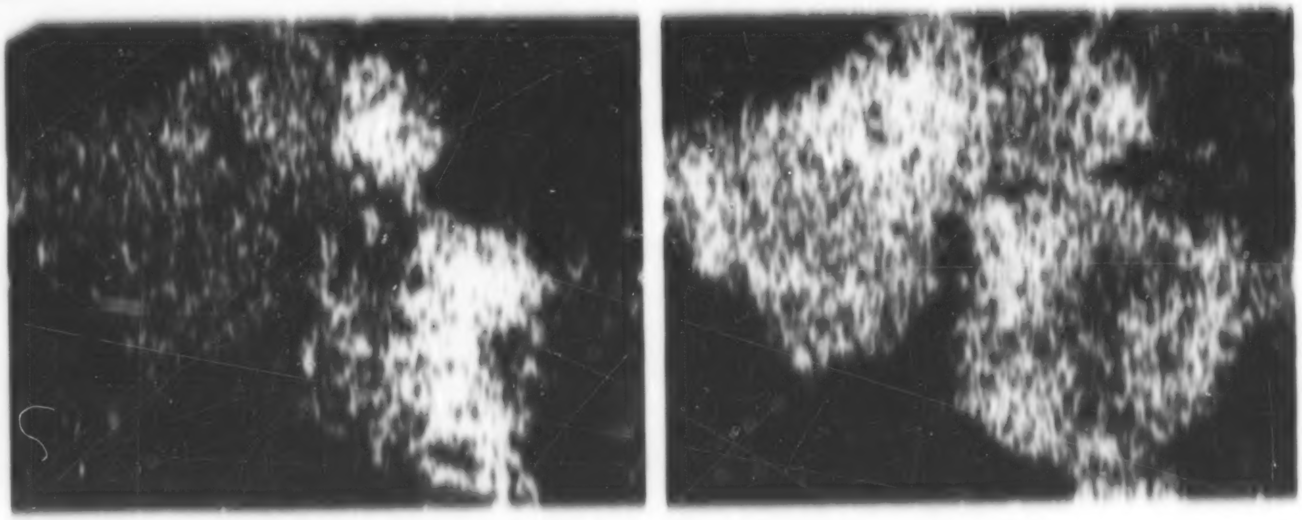
FIGURE XIV-5

Images of Sample A42-3 at 150X. Regenerator sample, 0.7 cycles, 25 mol % CaS.



Unspecific image,
reversed sample current

O X-ray

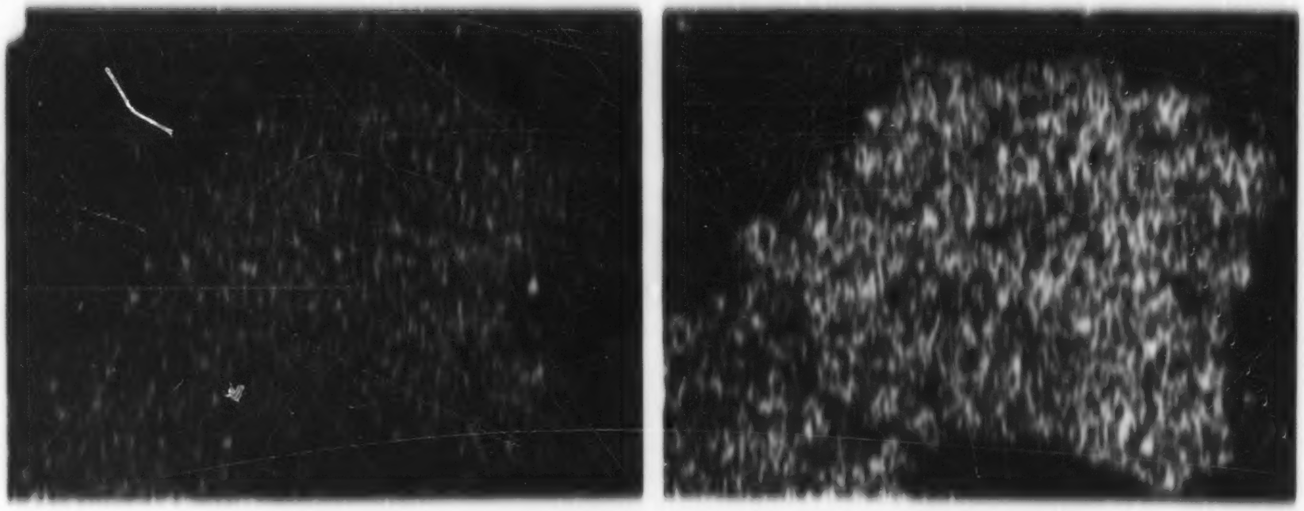


Mg X-ray

Ca X-ray

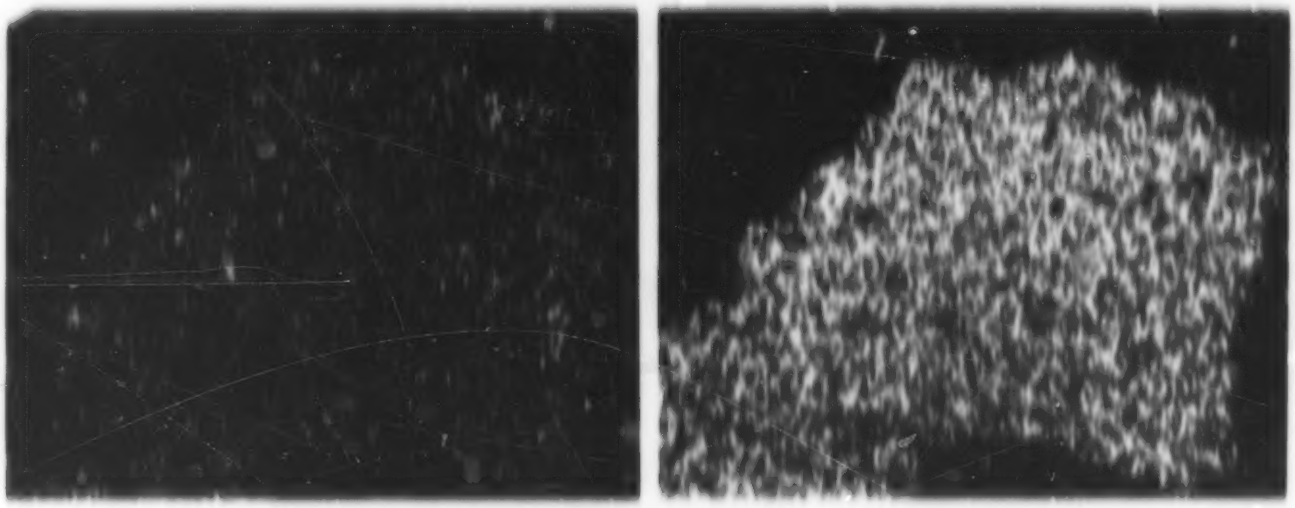
FIGURE XIV-6

Images of Sample A42-3A at 150X. Regenerator sample, 0.7 cycles, 25 mol % CaO.



Unspecific image,
reversed sample current

S X-ray



Mg X-ray

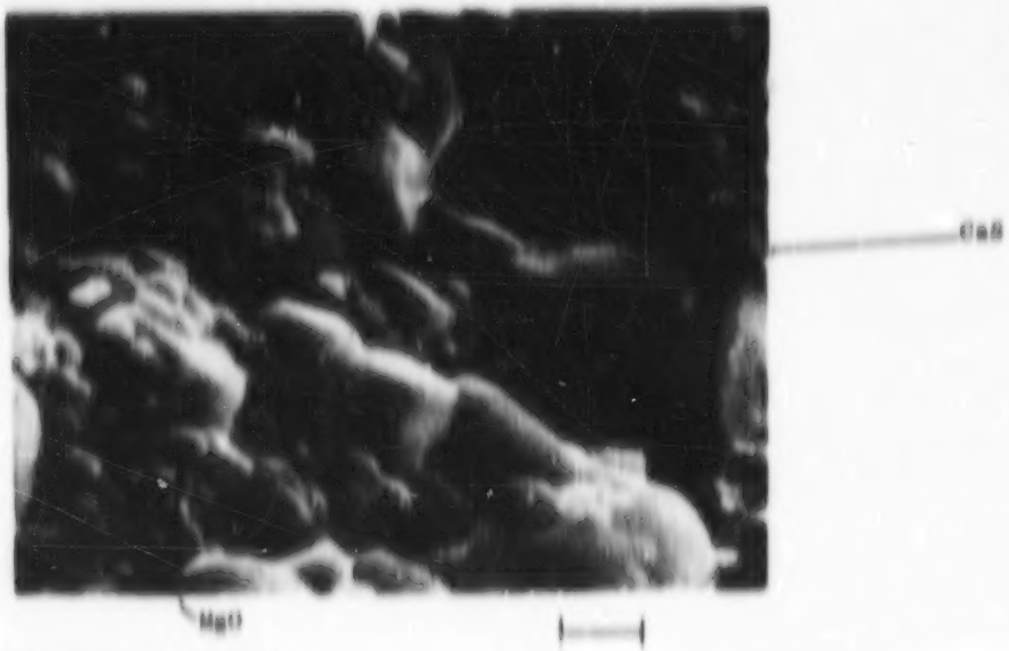
Ca X-ray

FIGURE XIV-7

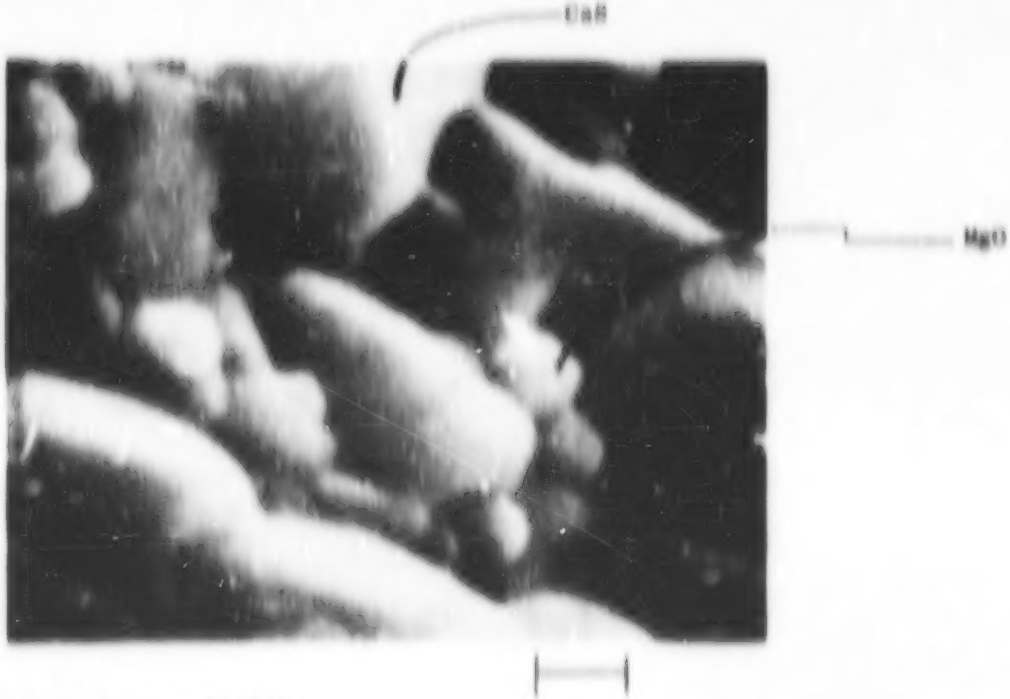
Images of Sample A40-4 at 150X. Regenerator sample, 9.6 cycles, 73 mol % CaS.

FIGURE XIV-8

SEM Photos of A78 Product



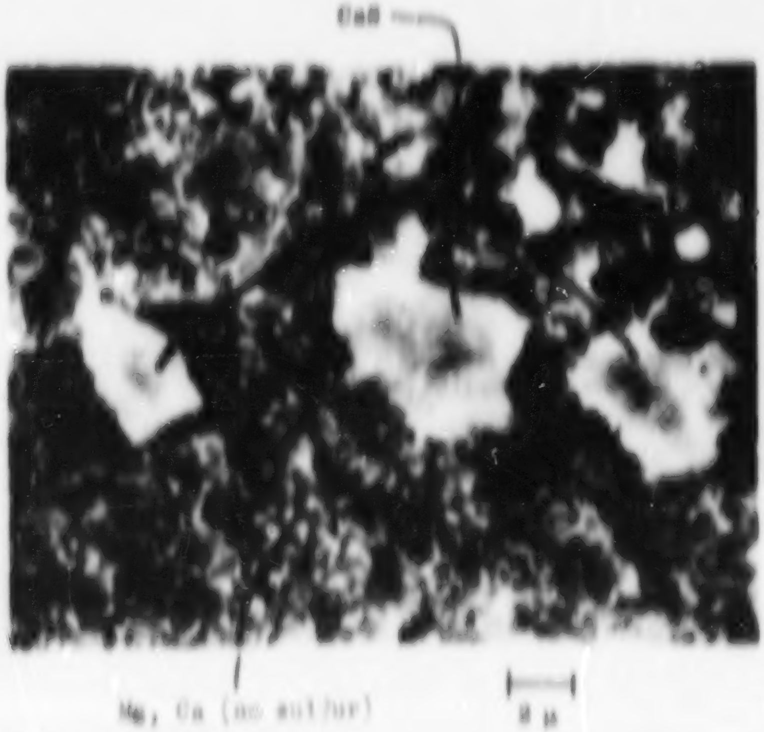
A. A78 Product x 25,000 0.4 μ



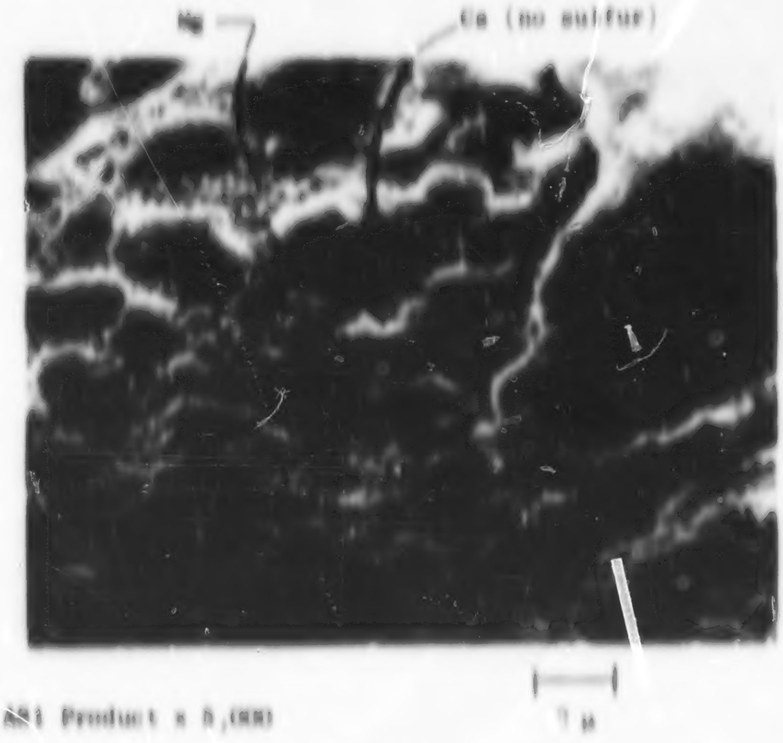
B. A78 Product x 71,000 0.14 μ

FIGURE XIV-9

SEM Photos of AR1 Feed and Product


CaS
Mg, Ca (no sulfur)
2 μ

A. AR1 Feed x 5,000

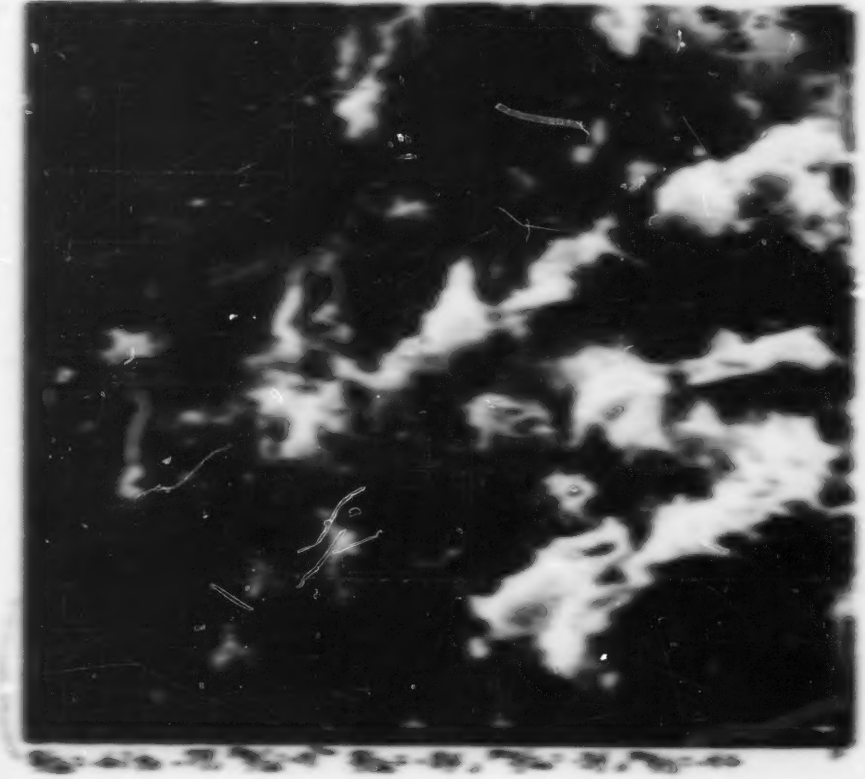

Mg
Ca (no sulfur)
2 μ

B. AR1 Product x 5,000

FIGURE [illegible]

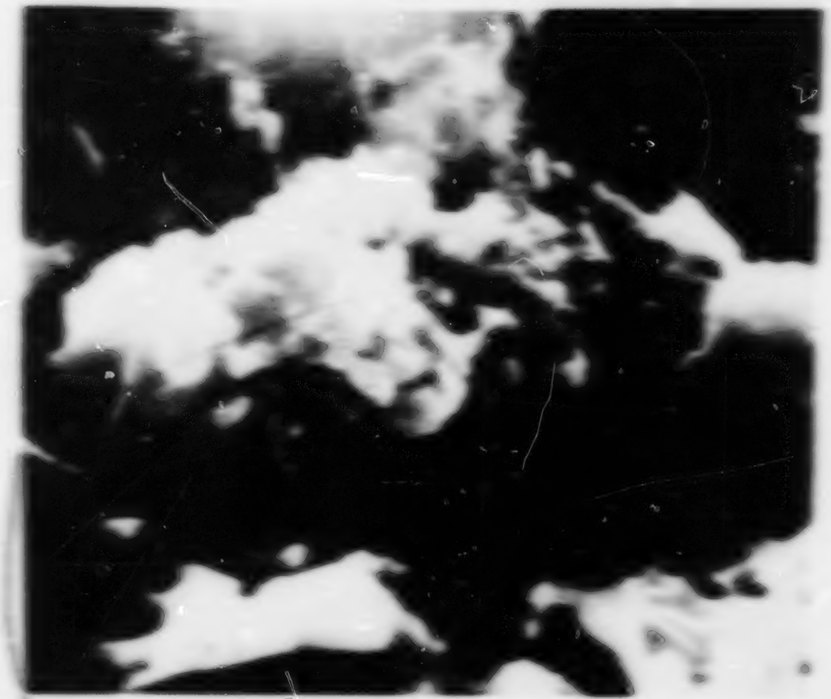
SEM Photos of [illegible] Bed
Elemental ratios given are relative rather than absolute

[illegible]



[illegible]

A. Interior Surface x 7750
Whole Area: S/Ca = .73, Mg/Ca = .37



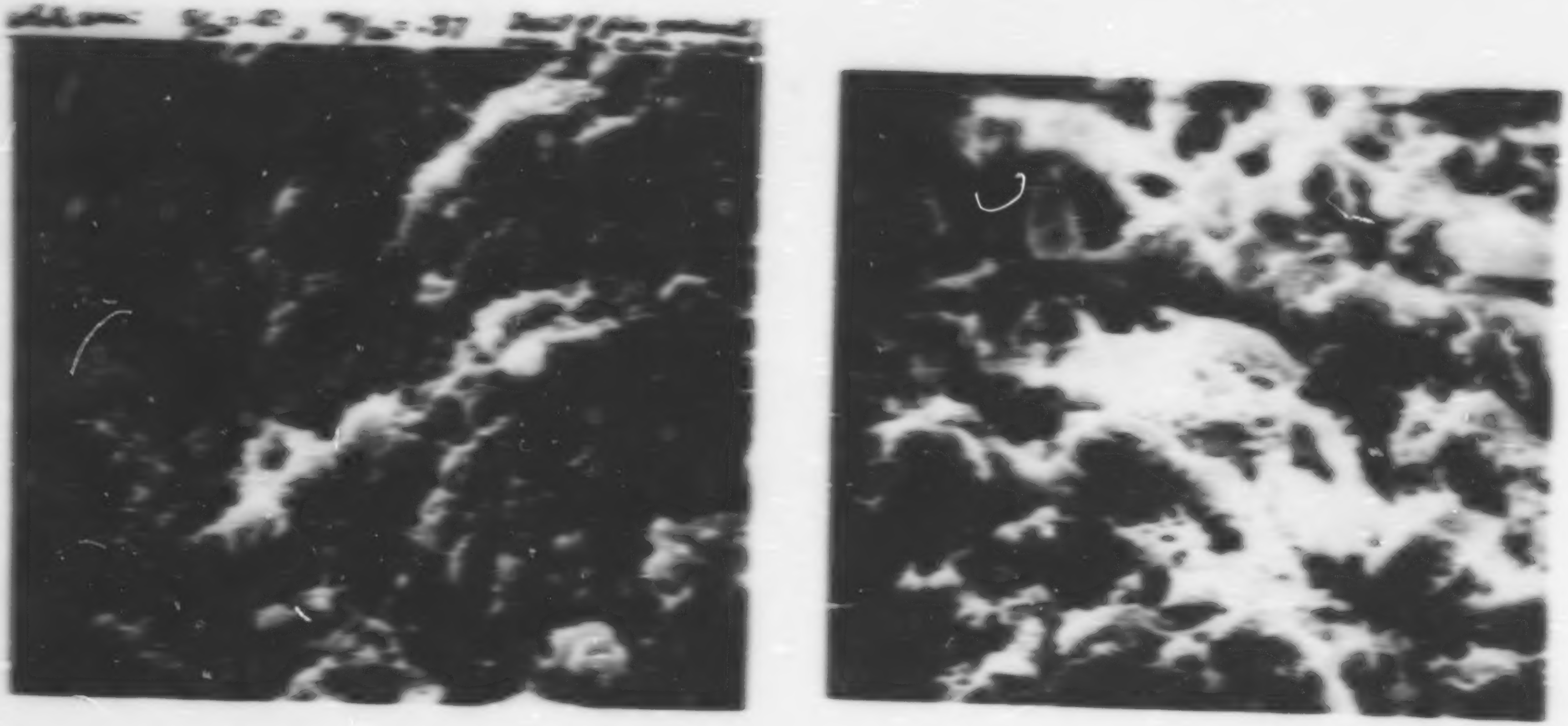
S/Ca = .79

B. Interior Surface, closeup of fine grained [illegible]
Whole Area: S/Ca = .67, Mg/Ca = .2

FIGURE XIV-11

SEM Photos of A46 Densification Bed

Elemental ratios given are relative rather than absolute



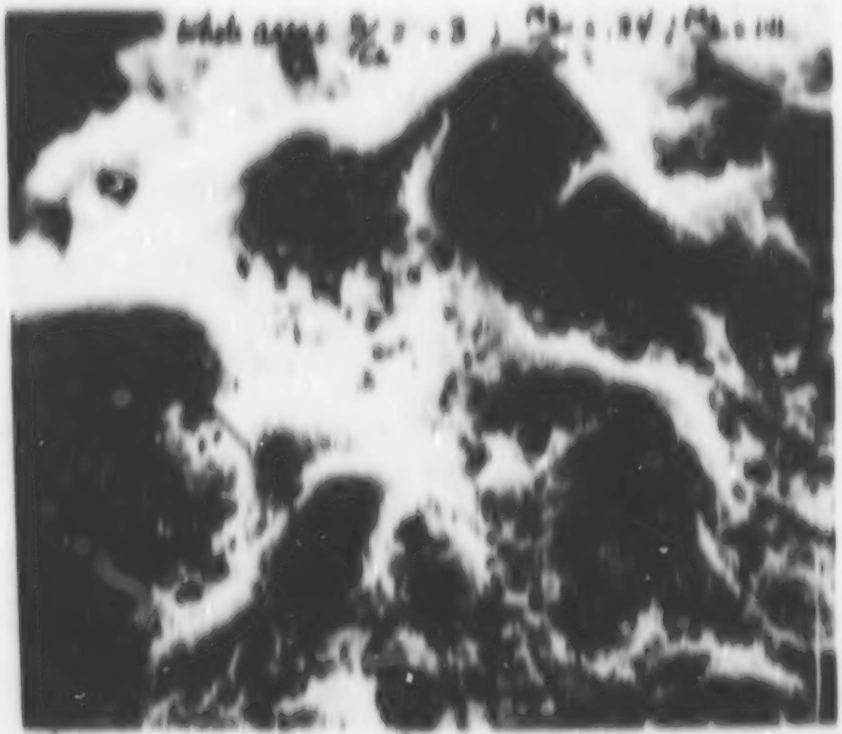
A. Fine Grained Area on Outer Surface x 6065
Whole Area: S/Ca = .51, Mg/Ca = .37

B. Fracture Surface (Interior of Particle) x 3000
Entire Area: S/Ca = .60, Mg/Ca = .32

FIGURE XIV-12

SEM Photos of A46 Desulfurizer Bed

Elemental ratios given are relative rather than absolute



white areas S/Ca = .8 ; Mg/Ca = .84 / [illegible]

Mg/Ca = .02 No sulfur
Hi Mg, Ca, Si

Mg/Ca = .41

External Surface x 3310
White Area: S/Ca = .8, Mg/Ca = .84

XV. SUMMARY OF VARIABLE EFFECTS

This section is a summary of the variable effects in the gas desulfurizer-regenerator system. The data relating to the system are scattered through a prior report and several sections of this report; this section is intended to tie them together and summarize them.

A. Gas Desulfurizer

Temperature - Increasing the temperature improves the desulfurization efficiency due to the improved equilibrium constant. Operation of the unit would also be affected if increasing temperature caused the equilibrium partial pressure of CO_2 needed to maintain the stone in the half-calcined state to exceed that in the gas stream thereby calcining the stone. As the temperature is increased, the allowable space rate, mols H_2S/hr-mol $CaCO_3$ in the bed, needed to prevent breakthrough increases. On the bench-scale equipment, the approach of the outlet gas to equilibrium improved as the temperature increased. However, it is noted that at 927°C (1700°F), the exit gas was at equilibrium, and the commercial unit is assumed to operate at equilibrium.

Conoco data on the effect of desulfurizer temperature on regeneration activity are sparse. In a previous study,(1) there was no effect in going from 871 to 899°C (1600-1650°F) in a short run. Data from the City College Clean Fuels Institute(14) indicate that increasing the desulfurization temperature from 800 to 900°C (1470-1650°F) reduces the regeneration activity, 100 x mols $CaCO_3$ produced/mol CaS fed, after 15 cycles from 9% to 4%.

Residence Time - There was no effect of solids residence time on the desulfurization step, however, increasing residence time produces a more severe deactivation of the stone with respect to the regeneration reaction. Experiments on the effect of gas residence time were confounded with bed height, but increasing gas residence time improved the approach to equilibrium.

Inlet H_2S Concentration - There is no effect of the inlet H_2S concentration since the outlet concentration is equilibrium controlled. However, the inlet H_2S concentration does affect the allowable H_2S:$CaCO_3$ space rate if all else is held the same.

Bed Height - Increasing the bed height improved the approach to equilibrium. However, the greatest effects were observed when the bed was reduced to only four inches. At that low level, bypassing may have been the controlling factor.

Particle Size - Over the range of 35 x 48 to 20 x 28 Tyler mesh there was no effect of particle size.

Age of $CaCO_3$ - There was no effect on desulfurization as the stone was cycled. As noted earlier, Westinghouse(13) had observed a 3% per cycle decline in rate of desulfurization in their system.

Type of Stone - All dolomites behaved about the same in the desulfurization step including the hardened stones. Limestones were not active in the desulfurization step.

B. Regenerator

Temperature - Temperature has an immense effect on the conversion of CaS to $CaCO_3$, the conversion increasing with temperature. The effect on equilibrium H_2S concentration is to decrease the H_2S as the temperature increases.

Residence Time - Conversion of solids increases with residence time, but the conversion rate drops markedly as a function of conversion at constant temperature.

Gas Concentration - There was no noticeable effect of variation of the inlet CO_2:H_2O ratio on the rate of reaction. Of course, the reactant concentration influences the ultimate concentration of product H_2S which is attainable within the equilibrium limitation. The role of H_2S is strange; data on hand suggest that increasing the inlet H_2S concentration allows the stone to reach a higher level of conversion.

Bed Height - Experiments with variation in bed height were confounded with effects of H_2S concentration and gas residence time. However, the effect was that increased bed height led to increased conversion and closer approach to equilibrium.

Particle Size - As in desulfurization, there was no effect of particle size.

Age of Stone - Without exception, the regeneration conversion fell as the stone was cycled. A log-log relation was found to exist between percent regeneration and number of cycles.

Type of Stone - Fresh dolomites displayed similar deactivation behavior. Hardened stones were sometimes less active than fresh ones depending upon the severity of the hardening process. Limestones were generally inactive.

Kinetic Model - The kinetic model, $Kt = - \ln (1 - X)$, is discussed fully in Section X and can be used to predict the effects of changes in residence time or temperature over a narrow range.

C. Model for the Deactivation Process

The regeneration reaction suffers from deactivation of the CaS even from cycle one. The model postulated below fits the behavior of the system so far. The part dealing with regenerator variables was developed jointly with City College Clean Fuels Institute.

Deactivation of the dolomite occurs mainly in the gas desulfurizer due to the elevated temperature. Two mechanisms are operating. Crystal growth of $CaCO_3$ and CaS segregates the calcium crystals from the MgO and produces a material tending toward a limestone rather than a dolomite. Simple sintering and densification take place as well, and this both hardens the stone and tends to reduce porosity. However, the observed changes in surface area and pore size are small compared to changes in activity.

In the regenerator, densification does not occur. However, the reaction starts rapidly and then tails off to an insignificant rate. Using the same feed, it can be shown that the conversion at which reaction essentially ceases is a strong function of temperature, the lower temperature producing the lower conversion. It has further been observed that introducing product H_2S does not retard the rate of reaction but conversely increases the ultimate level of conversion attainable.

The phenomenon of the products of reaction increasing the conversion of calcium in the sulfur-calcium system is not new. Pell[18] found that H_2O increased the conversion of CaO to CaS in the reaction of H_2S with calcined dolomite, and Ruth[19] showed that either CO_2 or H_2O could increase the conversion of $CaCO_3$ to CaS in the reaction of H_2S with half-calcined dolomite. Furthermore, both studies demonstrated the effect of the reaction flagging at lower and lower conversion levels as the reaction temperature decreased. Ruth[20] proposed the following mechanism after examination of electron microscope results on various samples. "High levels of CO_2..... may promote the formation of large number of fine crystallites of CaS that do not protect the underlying $CaCO_3$.... On the other hand, at low levels of CO_2 a smaller number of large CaS crystals form and grow together to close off the surface, thereby protecting the remaining $CaCO_3$ from further reaction."

Ruth's careful analysis of his data showed that in the presence of reaction products, the reaction was indeed slower initially. However, within a short time the conversion associated with the product-rich environment soon surpassed that in the product-poor environment.

It is postulated that a similar model fits the regeneration reaction. At low levels of H_2S, the $CaCO_3$ formed grows in large crystals shutting off the interior of the grain from further reaction. At high levels of H_2S, the reaction nucleates at many sites to produce many small crystals which leave the interior of the grain open to further reaction. Via such a mechanism, the presence of H_2S would enhance conversion in the regenerator. This is in full concordance with our experimental results.

XVI. DESIGN BASIS

This section contains a summary of the considerations entertained before selecting the specific design constraints used for the economic evaluation.

A. Gas Desulfurizer

The gas desulfurizer should be operated with the shortest possible residence time in order to maintain good regeneration activity of the dolomite sorbent. The previous residence time had been 30 minutes. Based on batch experiments, 30 minutes appeared completely sufficient to effect the required conversion. Since deactivation of the stone is thought to occur at the elevated temperature of the desulfurizer, the shorter time was chosen for the commercial design case. If it can be shown that the stone can be converted in a shorter time, the residence time might well be reduced further. The ultimate objective would be to desulfurize in an entrained-phase pipeline type of reactor. However, it has not been possible to set up an experiment to test this concept on the bench scale. Actual data on continuous runs have used a residence time on the order of 40-60 minutes. It is anticipated that going to the shorter residence time would ameliorate the decline in regeneration activity.

Four key factors affect the temperature of the gas desulfurizer: heat balance, deactivation, and equilibrium with respect to both H_2S removal and calcination of $CaCO_3$. In practice, the desulfurizer temperature is fixed by heat balance considerations between the hot fuel gas and the cooler stone from the regenerator. This worked out to be 1678°F (914°C) and is consistent with the other constraints.

The temperature of the bench-scale experiments was limited to 1600°F (871°C) by corrosion considerations, and the need to avoid excessive wall temperatures in the unit which might calcine the stone. Both from data and the model of deactivation, going to the design temperature of 914°C (1678°F) should result in more severe deactivation than would have been observed at 871°C.

For the design case, it was assumed that the deleterious effect of the higher temperature would be balanced by the ameliorating effect of the reduced residence time. The deactivation relationship used in the design was therefore the one experimentally determined for Canaan dolomite.

The makeup and circulation rates of dolomite sorbent were specified to maintain activity toward H_2S in the desulfurizer. The outlet H_2S concentration was assumed to be that determined from the equilibrium relationship. In order to achieve that equilibrium without breakthrough, a certain excess of $CaCO_3$ is required. It has been determined that the amount of excess was such that the H_2S:$CaCO_3$ molar hourly space velocity was a constant. Table XVI-1 is a summary of the data on this ratio for continuous runs in the bench-scale unit. The average ratio of 3.8 was chosen as the design constraint. This should be conservative since the gas residence time in the commercial vessel would exceed that in the bench-scale unit by several hundred percent. Using the ratio of 3.8, the H_2S feed rate and the 30 minute residence time as it affects the inventory of $CaCO_3$ in the unit, the makeup and conversion matrix shown in Table XVI-2 was calculated. This lists the acceptable design conditions for several stones of varying regeneration activity.

Preceding page blank

TABLE [illegible]

H_2S-$CaCO_3$ Ratio for Continuous Runs

Run No.	Mol % $CaCO_3$ at Break-through	Mols $CaCO_3$ in Reactor at Breakthrough	Mols/hr H_2S Feed	Mol Ratio, H_2S:$CaCO_3$, Hr^{-1}	Origin of Stone	Remarks
47	ca. 14	2.5	3.0	(ca. 1)[a]	Cannon 1	
[illegible]	4	0.72	3.0	4.1	Cannon 1	649°C (1200°F) regeneration
[illegible]	< 10	< 1.9	1.4	(> .7)	Cannon 2	No breakthrough
[illegible]	10	1.6	1.4	(0.9)	Tymochtee 10	982°C (1800°F) hardened
[illegible]	< 5	< .74	1.4	(> 1.8)	↓	No breakthrough
[illegible]	3	.40	1.5	3.6	↓	
[illegible]	2	.26	↓	5.9	↓	
[illegible]	ca. 2.5	.40	↓	3.8	Tymochtee 9	
[illegible]	2	.30	↓	5.0	↓	
[illegible]	4	.55	↓	2.8	↓	
[illegible]	5	.64	↓	2.4	Tymochtee 11	
[illegible]	2	.26	↓	6.3	↓	
[illegible]	5	.73	↓	2.1	Buchanan 3	
[illegible]	3	.48	↓	3.2	↓	
[illegible]	4	.50	1.0	2.0	Tymochtee 11	
[illegible]	3.5	.45	1.0	2.3	↓	
[illegible]	< 2	< .26	0.55	(> 2.1)	↓	No breakthrough
[illegible]	2	.32	1.0	3.1	Buchanan 3	
[illegible]	3	.50	2.0	3.5	Cannon 3	
				3.6 average		

(a) Numbers in parentheses were not included in the evaluation of the average.

The choice was made on the basis of conservatism with respect to the possibility of the attrition rate exceeding 1%. A 1% makeup rate would be desirable from considerations of makeup cost and the cost of the disposal train. However, since the total process cost increases by only about 5% for each 1% increase in makeup acceptor, the 2% level was chosen. This permits a greater variety of natural stones to be employed without having to resort to a hardening step. A finding to the effect that natural stones were prevalent which could indeed be used with an attrition rate below 1% would lead to the reinstatement of the 1% makeup rate as the design basis.

B. Regenerator

Residence time in the regenerator was chosen as 60 minutes, essentially the same time which had been employed in the experimental continuous runs. The temperature of 704°C (1300°F) was a compromise between two factors. If the temperature were higher, increased conversion to $CaCO_3$ could be obtained. However, the equilibrium H_2S concentration would be reduced and we would require a larger liquid-phase Claus system. Reducing the temperature would yield a higher equilibrium H_2S concentration at the cost of reduced conversion of stone. An optimization was not carried out, and the design temperature is an estimate of what would give a reasonable result.

In bench-scale runs, the equilibrium H_2S concentration was obtained in the outlet gas on at least one occasion, and all the data pertaining to approach to equilibrium in the regenerator indicate that approach to equilibrium should present no problem. In fact, higher H_2S concentrations may enhance the attainable conversion beyond what had been observed in the continuous unit. As there would be little change in the design by raising the previous estimated approach to equilibrium of 88%, the same number was retained for the present design.

C. Tertiary Particulate Removal

The tertiary particulate removal system was sized and costed as a cyclone. While it is recognized that a more elaborate system may be required, work in this area is not sufficiently advanced to warrant design of a particular alternative. It is expected that the efforts underway in the area of pressurized fluidized bed combustion will eventually result in workable high temperature tertiary particulate removal system. Its substitution for the hot cyclone assumed here should not markedly affect the overall economics.

TABLE XVI-2

Stone Makeup Summary
Regenerator Temperature = 704°C (1300°F)

Material	Makeup Rate, % of Circulation	Conversion, Mols CaS Formed / 100 Mols Ca Fed to Desulfurizer	Equilibrium, Mols $CaCO_3$ / 100 Mols Ca Fed to Desulfurizer	Mol Ratio, CaS Makeup: H_2S Absorbed
Canaan Dolomite	1.0	8.9	16.9	.11
	1.5	10.4	19.1	.13
	2.0	11.7	21.4	.17
Hardened Tymochtee Dolomite	1.0	8.0	14.6	.13
	1.5	8.9	16.3	.17
	2.0	9.7	17.9	.21
Hardened (95%) Buchanan Dolomite	1.0	7.5	13.7	.13
	1.5	8.6	15.7	.18
	2.0	9.5	17.4	.22

XVII. ENVIRONMENTAL EVALUATION

Introduction

The purpose of this evaluation is to describe the impact of the desulfurization process on the environment. The integration of the desulfurization process into the coal gasification and power plant scheme is depicted in Figure XVII-1. The quantity of materials consumed and generated is reported in tons/year (8132 operating hours). It must be emphasized that even though this is an integrated process, the scope of this environmental evaluation is limited to the desulfurization processing step. Refer to CCIE Drawing AF-3867 in Section III for more detail of the proposed process.

Thermal Efficiency

Since thermal efficiency measures efficiency of resource utilization, it is a key environment factor. As used herein, thermal efficiency is the percentage of the total input heating value (feed gas plus external fuel) that is recovered as net product (producer gas to power plant) and by-product heating value (gasifier steam and sulfur). As calculated from the overall mass and heat balance (Table III-8), the process has a thermal efficiency of 95.8%. The high thermal efficiency is the single most important attribute of this desulfurization process.

Waste Generation

About 0.14 million TPY of spent dolomite will be generated from the desulfurization process for deposit in a slurry pond. To date, a process to recover and recycle dolomite from its attrited sludge form has not been developed. On the other hand, there are several outlets for the dolomite sludge. The material can be used for land fill since it has the same basic chemical constituents as in the original quarry stone. Other potential markets include road fill material, cement production, and agricultural lime.

Make-up dolomite is calcium magnesium carbonate with some inert noncarbonate compounds such as clay, silica and silt. Trace elements in the dolomite will vary with the stone type and source. Typical trace elements and oxides for Illinois limestone and dolomite are listed in Tables XVII-1 and XVII-2(51) below. The morphology of the trace elements through the process and the potential impact of their final state on the environment have not been studied.

TABLE XVII-1

Trace Elements in 90 Illinois Limestone Samples

Trace Element	Amount (% by Wt.)	Trace Element	Amount (% by Wt.)
Barium	0.0080	Nickel	0.0015
Boron	0.0018	Potassium	0.18
Chromium	0.0011	Sodium	0.07
Copper	0.0018	Strontium	0.049
Iron	1.13	Titanium	0.04
Lead	0.0030	Vanadium	*
Manganese	0.14	Zinc	0.004
Molybdenum	0.0001		

* Present as trace in only three samples.

FIGURE XIII-1

Process Flow Schematic

Materials Consumed and Generated (Tons/Year)

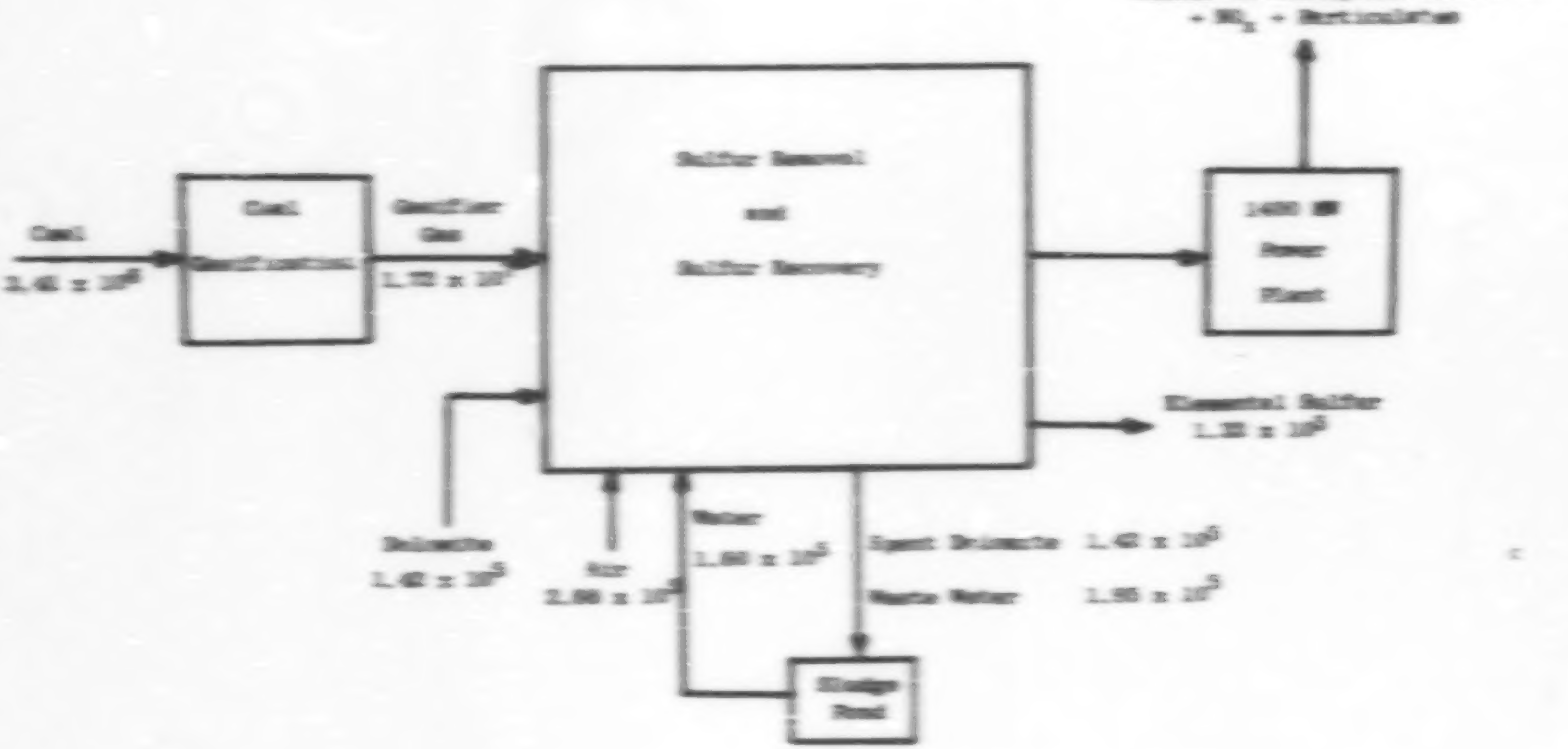

Coal
1.41 x 10^6
Coal Gasification
Gasifier Gas
1.72 x 10^7
Sulfur Removal
and
Sulfur Recovery
1400 MW
Power
Plant
Sulfur to Atmosphere 6.44 x 10^3
+ NO_x + Particulates
Elemental Sulfur
1.33 x 10^5
Dolomite
1.42 x 10^5
Air
2.88 x 10^5
Water
1.60 x 10^5
Spent Dolomite 1.42 x 10^5
Waste Water 1.95 x 10^5
Sludge
Pond

TABLE XVII-3

Phosphorus Pentoxide, Manganese Oxide, and Sulfur Trioxide in Illinois Limestones and Dolomites Containing More than 95 Percent Carbonates

	No. of Samples	Average (%)	Range (%)
Phosphorus Pentoxide (P_2O_5)			
Limestone	26	.029	.004-.097
Dolomite	16	.006	.000-.032
Manganese Oxide (MnO)			
Limestone	12	.015	.002-.044
Dolomite	14	.040	.010-.050
Sulfur Trioxide (SO_3)			
Limestone	29	.13	.03-.88
Dolomite	39	.17	.02-.50

Elemental Sulfur

The elemental sulfur product of 1.32 x 10^5 short tons per year will be marketed at a substantial dollar credit to the process. Consequently, there is no disposal problem associated with the sulfur.

Water Use

About 1.80 x 10^5 tons per year of recycle pond water are required for the cooling and conversion of reject acceptor. In addition, annual cooling water make-up requirements total approximately two million tons or 1500 acre-feet.

Noise and Dust

Without a detailed design, noise and dust levels are difficult to predict. If crushing and sizing of the dolomite is done on the plant site, some noise and dust will be generated with the feeder and milling operations. Also, the process includes several large compressors which must be designed to meet OSHA noise levels. These areas must be considered with other pertinent design criteria.

Emissions from the Power Station

A rigorous review of the environmental evaluation of the power station using the desulfurized gas is beyond the scope of this study. However, since the atmospheric emissions of the power plant are a direct function of the incoming gaseous fuel quality, the impact of the desulfurization process on the producer gas quality will be discussed here.

The Clean Air Amendments of 1970 have resulted in the promulgation of air quality control regulations covering emissions from new stationary sources which contribute significantly to air pollution, or cause or contribute to the endangerment of public health and welfare. For a coal-derived, gas-fuel-burning installation rated at 250 x 10^6 Btu/hr input or greater, the "new source" emission standards expressed in pounds per million Btu of input fuel are as follows: Sulfur dioxide - 1.20; particulate matter - 0.10; and nitrogen oxides - 0.20. Although a number of states and local communities have adopted more stringent specifications, this discussion is limited to the general standards.

Sulfur Oxides Pollution

The basic purpose of this study is to desulfurize a low-Btu coal-derived gas for fuel to power stations. The total sulfur in the producer gas (including the vent gas from the SO_2 absorption column) is equivalent to approximately 20% of the 1.20 lb/MM Btu input sulfur dioxide emission standard.

Particulates

The state of the art in particulate removal technology at elevated temperatures has advanced markedly in the past several years.(7,11) The incentive to develop this area has not been for environmental reasons alone. To permit greater utilization efficiency of our coal resources, considerable development work is being done on the low Btu gas combined cycle. Hot fuel gas filtration is necessary to protect the gas turbine components of the combined cycle power system. In fact, the turbine specifications for particulate matter are generally more stringent than the environment "new source" standards.

The proposed design scheme includes three stages of particulate collection. First, the desulfurized gasifier gas passes through two stages of cyclones to remove substantially all of the fines including attrited acceptor and entrained ash. After heat exchange to generate steam for coal gasification, the gas is sent through a third stage particulate collector to remove any potential alkali compounds formed at the lower gas temperatures and to serve as a final process clean-up step. To maximize efficiency, the second and third stages can be operated at high pressure drops due to the inherent high pressure of the producer gas.

Preliminary experimental results have shown no traces of alkali-bearing compounds in the gas once all the particulate matter has been removed at 704°C (1300°F). It is theorized that the particulate matter serves as nuclei for alkali deposition. Consequently, removal of particulates eliminates any potential alkali problem. Further work is needed to confirm these preliminary results.

Nitrogen Oxides Pollution

All high temperature combustion processes of fossil fuels with air result in the formation of nitrogen oxides (NO_x). Nitrogen oxides will be formed in the high temperature combustion zone by the direct reaction of atmospheric oxygen with atmospheric nitrogen and with nitrogen containing compounds in the fuel. In the producer gas from coal gasification the nitrogen-bearing compounds include about 47% nitrogen and about 0.23% ammonia. One disadvantage of the hot gas cleanup process is that the ammonia is not removed. This will effect an increase in the NO_x emissions from the power plant.

The level of ammonia conversion to NO_x in the power plant cannot be predicted with any degree of certainty. The results of laboratory experiments and furnace studies indicate a low conversion, i.e., less than 30%.(8,15)

However, the results have not been confirmed under power plant conditions. Furthermore, experimental work at low ammonia concentrations (less than 1%) is very limited. The potential impact of various ammonia conversion levels on NO_x is shown below:

% Ammonia Conversion to NO_x	NO_x Level (lb/MM Btu of Coal Input)
2	0.04
10	0.19
50	0.95

At any conversion level above 37% the "new source" standard of 0.7 lb/MM Btu of fuel input is exceeded by the ammonia contribution alone.

Based on the results of laboratory experiments and furnace plant tests,(8,10) it appears the conversion of ammonia to NO_x can be limited by the same principles as presently applied to control NO_x emissions from gas, oil, and coal-fired utility steam generators.(9,11) Typical control techniques include staged combustion (also known as "over-fire air simulation" or "off-stoichiometric combustion"), flue gas recirculation and water injection. These methods result in varying (1) reductions of NO_x emissions, (2) degradation in boiler efficiency, and (3) yields of other emissions such as carbon monoxide.

In the case of gas turbine combustion systems, NO_x levels have been reduced by 85% by either direct water injection in the combustor primary zone or by adding steam to the combustion air.(12) In the first method, further benefits included a marked reduction in smoke and a net increase in turbine power.

In conclusion, assuming the ammonia conversion to NO_x can be controlled at a relatively low level, i.e., less than 10%, then it appears that the principles and techniques required to achieve NO_x specifications are relatively well known. This is true whether the conventional gas burning power station or the gas turbine of the advanced combined cycle burns the fuel gas. As indicated previously, a thorough investigation of the level and control of NO_x emissions from the power station is beyond the scope of this study.

XVIII - REFERENCES

1. Curran, G.P., Clancey, J.T., Pasek, B., Pell, M., Rutledge, G.D., and Gorin, E., "Production of Clean Fuel Gas from Bituminous Coals," Report to Office of Research & Development, U. S. Environmental Protection Agency, Under Contract EHSD 71-15, Period: March, 1972 to June, 1973, EPA Report No. 650/2-73-049, NTIS No. PB 232-695/AS.

2. Curran, G.P., Clancey, J.T., Fink, C.E., Pasek, B., Pell, M., and Gorin, E., "Development of the CO_2 Acceptor Process Directed Towards Low-Sulfur Boiler Fuel," Annual Report to Control Systems Division, Environmental Protection Agency, Under OAP Contract EHSD 71-15, Period: Sept. 1, 1970 to Nov. 1, 1971, NTIS Accession No. PB 210-840.

3. Robson, F.L., Giramonti, A.J., Lewis, G.P., Gruber, G., "Technology and Economic Feasibility of Advanced Power Cycles and Methods of Producing Nonpolluting Fuels for Utility Power Stations," United Aircraft Research Laboratories Report No. J-970855-13, Dec., 1970, Under NAPCA Contract CPA 22-69-114.

4. Sherwood, T.K., Ind. Eng. Chem., 17, 745 (1925).

5. Adams, F.W., Trans. Am. Inst. Chem. Engrs., 25, 424 (1933).

6. Matell, S., and Faber, J.H., Petr. Ref., 39, No. 3, 187-190 (1960).

7. Stone and Webster Engineering Corp., "Purification of Hot Fuel Gas From Coal or Heavy Oil," Interim Report to Electric Power Research Institute, EPRI 243-1, Nov., 1974.

8. Wendt, J.O.L., and Sternling, C.V., (Shell Development Co.), "Effect of Ammonia in Gaseous Fuels on Nitrogen Oxide Emissions," Journal of Air Pollution Control Association, Vol. 24, No. 11, Nov., 1974.

9. Blakeslee, C.E., and Burbach, H.E., (Combustion Engineering), "Controlling NO_x Emissions from Steam Generators," 65th Annual Meeting of the Air Pollution Control Association, Miami Beach, June, 1972.

10. Beychok, M.R., (Fluor Engineers & Contractors, Inc.), "NO_x Emission From Fuel Combustion Controlled," The Oil and Gas Journal, 71, No. 9, 53-56, Feb. 26, 1973.

11. Curran, G.P., Fink, C.E., and Gorin, E., "Phase II, Bench-Scale Research on CSG Process, Operation of the Bench-Scale Continuous Gasification Unit," Office of Coal Research R&D Report No. 16, Interim Report No. 3, Book 3, GPO Catalog No. I63.10:16/INT3/Book 3 (1969).

12. Hicks, C.R., "Fundamental Concepts in the Design of Experiments," Holt, Rinehart and Winston, New York (1965).

13. O'Neill, and Keairns, D.L., "Selection of Calcium-Based Sorbents for High-Temperature Fossil Fuel Desulfurization," Paper presented at AIChE Meeting, Boston, Sept. 7-10, 1975.

Preceding page blank

14. Squires, A.M., City University of New York, Personal Communication, Oct., 1975.

15. Rao, C.P., and Gluskoter, H.J., "Occurrence and Distribution of Minerals in Illinois Coals," Circular 476, Illinois State Geological Survey, Urbana, Ill. (1973).

16. Keairns, D.L., Archer, D.H., et al., "Fluidized Bed Combustion Process Evaluation, Phase II - Pressurized Fluidized Bed Coal Combustion Development." EPA Report No. EPA-650/2-75-027C (1975).

17. Chance, A.M., "The Recovery of Sulphur and Alkali Waste by Means of Lime Kiln Gases," *J. Soc. Chem. Ind.*, 163-179, March 31, 1888.

18. Pell, M., "Reaction of Hydrogen Sulfide with Fully-Calcined Dolomite," Ph.D. Thesis, The City University of New York (1971).

19. Ruth, L.A., Squires, A.M., and Graff, R.A., "Desulfurization of Fuels with Half-Calcined Dolomite: First Kinetic Data." Env. Science & Tech., *6*, 1009-1016 (1972).

20. Ruth, L.A., "Reaction of Hydrogen Sulfide with Half-Calcined Dolomite," Ph.D. Thesis, The City University of New York (1972).

21. Lamar, J.E., Handbook on Limestone and Dolomite for Illinois Quarry Operators, Bulletin 91, Illinois State Geological Survey, Department of Registration and Education, 1967.

22. Westinghouse Research Laboratories, Report to the Office of Air Programs, Environmental Protection Agency, under Contract No. CPA 70-9 (1971); Volume III, Appendix H.

23. Bartok, et al., Esso Research and Engineering Company, "Systematic Field Study of NO_x Emissions Control Methods for Utility Boilers." Environmental Protection Agency, under Contract No. CPA 70-90, National Technical Information Service PB 210-739, Dec. 31, 1971.

24. Singh, et al., Westinghouse, "Formation and Control of Oxides of Nitrogen Emissions from Gas Turbine Combustion System." ASME Paper No. 72-GT-22, March, 1972.

25. JANAF Tables, Dow Chemical Company, Clearinghouse for Federal Scientific and Technical Information, U.S. Dept. of Commerce, No. PB 168-370 (1965) and No. PB 168-370-1 (1966).

26. Preuner, G., and Schupp, W., *Z. Physik. Chem.*, *68*, 129 (1909).

27. West, J.R., *Ind. Eng. Chem.*, *42*, 713 (1950).

28. Curran, G.P., Fink, C.E., and Gorin, E., "CO_2 Acceptor Gasification Process - Studies of Acceptor Properties," in "Fuel Gasification," *Advances in Chemistry Series No. 69*, ACS, Washington, D.C. (1967).

29. Zawadzki, J., *Z. Anorg. Chem.*, *205*, 180 (1932).

30. Hill, K.J., and Winter, E.R.S., "Thermal Dissociation Pressure of Calcium Carbonate," *J. Phys. Chem.*, **60**, 1361-1362 (1956).

31. Uno, T., *Tetsu to Hagane*, **37**, 16-17 (1951).

32. Rosenqvist, T., "A Thermodynamic Study of the Reaction $CaS + H_2O = CaO + H_2S$ and the Desulfurization of Liquid Metals with Lime," *J. Metals Trans.*, AIME, 3, 535-540 (1951).

33. Batchelor, J.D., Yavorsky, P.M., and Gorin, E., *J. Chem. & Eng. Data*, **4**, (3), 241 (1959).

34. Terres, E., and Schaller, A., *Gas and Wasserfach*, **65**, 761 (1922).

35. Batchelor, J.D., CCDC unpublished data.

36. Lisauskas, R.A., and Johnson, S.A., *Chem. Eng. Prog.*, **72**, (8), 76-77, (1976).

Appendix A

Detailed Investment Costs

Preceding page blank

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		
		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]		[illegible]						[illegible]
[illegible]		[illegible]		[illegible]	[illegible]				[illegible]	
[illegible]		[illegible]		[illegible]	[illegible]			[illegible]		
[illegible]		[illegible]		[illegible]	[illegible]		[illegible]			
[illegible]		[illegible]		[illegible]	[illegible]	[illegible]				
[illegible]		[illegible]		[illegible]	[illegible]					
[illegible]		[illegible]		[illegible]	[illegible]					
[illegible]		[illegible]		[illegible]	[illegible]					
		[illegible]		[illegible]	[illegible]					
		[illegible]		[illegible]						
[illegible]				[illegible]						
		[illegible]		[illegible]						

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] [illegible]		[illegible]		[illegible]						[illegible]
[illegible]		[illegible]		[illegible]	[illegible]				[illegible]	
[illegible]		[illegible]		[illegible]	[illegible]			[illegible]		
[illegible]		[illegible]		[illegible]	[illegible]		[illegible]			
[illegible]		[illegible]		[illegible]	[illegible]	[illegible]				
[illegible]		[illegible]		[illegible]	[illegible]					
[illegible]		[illegible]		[illegible]	[illegible]					
[illegible]		[illegible]		[illegible]	[illegible]					
		[illegible]		[illegible]	[illegible]					
		[illegible]		[illegible]						
[illegible]				[illegible]						
		[illegible]		[illegible]						

APPENDIX B

Data Tables

Detailed tables of data obtained during the program described in the report are contained in this section. They are:

- B-1 Composition of Exit Solids from Cycling Runs
- B-2 H_2S Content of Exit Solids from Cycling Runs
- B-3 Attrition Data
- B-4 H_2S Content of Exit Gas - Batch Variable Studies

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

TABLE B.1 (Cont'd.)

Composition of Salt Solids from Cycling Runs

TABLE B-1 (Cont'd.)

Composition of Bed Solids from Cycling Runs

Run No.	Gas Desulfurizer				Regenerator			
		Mol %				Mol %		
	Cycle No.	$CaSO_4$	CaS	"CaO"	Cycle No.	$CaSO_4$	CaS	"CaO"
A37	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible] min	[illegible]	[illegible]	[illegible]
A38	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible] min	[illegible]	[illegible]	[illegible]
A41	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible] min	[illegible]	[illegible]	[illegible]
A42					[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible] min	[illegible]	[illegible]	[illegible]
A43	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A44A	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible] min	[illegible]	[illegible]	[illegible]
A45	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible]	[illegible]	[illegible]	[illegible]
					[illegible] min	[illegible]	[illegible]	[illegible]
A46	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE D-1 (Cont'd.)

Composition of Salt Solids from Cycling Runs

Run No.	Cycle No.	Gas Desulfurizer Mol % $CaCO_3$	CaS	"CaO"	Cycle No.	Regenerator Mol % $CaCO_3$	CaS	"CaO"
A47	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
					[illegible] + 105 min	[illegible]	[illegible]	[illegible]
A48	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A51	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A52	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
A102	1 (feed)	[illegible]	[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]
	2	[illegible]	[illegible]	[illegible]	2	[illegible]	[illegible]	[illegible]
	3	[illegible]	[illegible]	[illegible]	3	[illegible]	[illegible]	[illegible]
	4	[illegible]	[illegible]	[illegible]	4	[illegible]	[illegible]	[illegible]
A104	1	[illegible]	[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]
A106	1 (feed)	[illegible]	[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]
	2	[illegible]	[illegible]	[illegible]	2	[illegible]	[illegible]	[illegible]
	3	[illegible]	[illegible]	[illegible]	3	[illegible]	[illegible]	[illegible]
	4	[illegible]	[illegible]	[illegible]	4	[illegible]	[illegible]	[illegible]
A109	1	[illegible]	[illegible]	[illegible]				
	2	[illegible]	[illegible]	[illegible]	2	[illegible]	[illegible]	[illegible]
	3	[illegible]	[illegible]	[illegible]	3	[illegible]	[illegible]	[illegible]
	4	[illegible]	[illegible]	[illegible]	4	[illegible]	[illegible]	[illegible]

TABLE B-1 (Cont'd.)

Composition of Bed Solids from Cycling Runs

Run No.	Cycle No.	Gas Desulfurizer Mol % $CaCO_3$	CaS	"CaO"	Cycle No.	Regenerator Mol % $CaCO_3$	CaS	"CaO"
A100A	1	72.8	10.9	16.9	1	81.5	0.7	16.9
	2	69.5	16.8	13.7	2	74.0	11.3	14.7
	3	57.8	24.5	17.7	3	66.8	17.3	15.9
	4	51.9	31.1	16.9	4	60.9	23.4	15.7
	5	41.9	40.4	17.7	5	51.5	30.0	18.5
	7	34.0	47.6	18.5	7	40.0	35.4	20.5
	9	17.8	65.8	16.6	9	31.6	47.5	20.9
	11	7.8	75.5	16.7	11	30.7	50.5	18.8
A100	1	73.7	11.1	15.2	1	80.6	9.1	8.8
	2	72.8	11.0	15.5	2	67.5	8.5	10.5
	3	71.5	11.9	16.6	3	66.8	8.4	10.9
	5	68.0	16.6	15.4	5	62.0	8.1	12.0
	7	62.9	17.5	19.6	7	73.5	6.9	15.8
	9	56.5	25.1	18.1	9	70.8	13.5	15.9
	11	48.3	33.6	17.8	11	65.4	19.9	14.7
A101	1	60.6	24.4	15.0	1	78.6	7.6	13.7
	2	47.3	35.5	16.9	2	66.0	21.3	12.7
	3	37.0	47.5	15.5	3	57.4	28.1	13.8
	5	9.8	78.7	11.5	5	35.5	54.0	10.5
	7	5.5	75.8	19.5	7	17.4	62.3	19.4
	9	2.5	77.8	20.0	9	16.1	64.8	18.7
	11	1.4	79.7	18.9	11	13.0	66.5	18.8
A102	1	53.7	29.5	16.7	1	76.5	9.1	14.4
	2	52.7	35.4	12.0	2	64.0	21.7	14.6
	3	28.7	54.1	17.3	3	53.1	31.8	15.7
	5	10.7	71.9	17.4	5	30.7	53.6	15.7
	7	1.8	82.6	15.6	7	25.6	62.7	11.7
	9	16.3	66.0	17.7	9	25.0	56.9	18.8
	11	5.0	78.7	16.3	11	22.3	61.6	16.3

TABLE B-2

H_2S Content of Exit Gas from Cycling Runs
Dry Basis

Run No.	Cycle No.	Mol % H_2S from Regenerator	Mol % H_2S from Gas Desulfurizer, % [illegible]
A20A	1.0	.88	.03
	1.8	.88	.03
	6.9	.84	.03
	9.9	.83	.03
	10.4	.86	.03
	14.4	.78	
	18.1	.88	
	22.6	.88	
	23.4	.88	
	26.4	.80	.03
	30.0	.82	.03
	31.8	.80	.03
A21	3.8	2.61	.03
	5.9	2.46	.03
	6.9	2.07[a]	0.1[a]
	8.8	2.80	.03
	10.4	2.10	
	15.8	2.71	
	18.0	2.84	
	19.0	2.9[a]	0.1[a]
	22.8	2.44	.03
	25.4	2.48	
	28.7	2.41	
	32.1	2.84	
	33.0	2.02[a]	0.1[a]
	35.8	2.10	.03
	36.7	2.08	.03
A22A	3.8	1.00	.03
	5.8	.98	.03
	6.8	1.00	.03
	7.7	.98	.03
	10.8	.84	
	13.8	.84	
	17.0	.88	
	18.8	.88	
	22.0	.88	
A23	0.7	2.4	.03
	1.0	1.03	.03
	1.7	1.3	.04
	3.1	1.08	.03
	5.8	3.03[a]	0.1[a]
	8.0	2.1	.04
	9.4	2.1	.08
	10.8	2.00	.18
	12.8	3.0	.12
	14.0	4.31	.08
	15.0	4.20[a]	0.1[a]
	18.0	1.18	.08
	22.1	.84	.34
	23.1	.76[a]	.32[a]
A24	1.1	1.9	.03
	3.0	1.8	
	4.0	1.38	
	5.0	1.28	
	7.0	1.24	
	9.0	1.43	.03
	11.0	1.43	.03
	11.8	1.40[a]	0.1[a]
	14.4	1.44	.20
	16.9	1.30	.08

[a] [illegible] analysis. Other numbers are via ultraviolet absorption.

TABLE B-8 (Cont'd.)

H_2S Content of Spent Gas from Cycling Runs
Dry Basis

Run No.	Cycle No.	Mol % H_2S from Regenerator	Mol % H_2S from Gas Desulfurizer, ≤ .01%
A25	0.8	2.10	.04
	3.4	1.85	.03
	5.5	1.98	↓
	7.8	1.06	↓
	10.0	1.16	↓
	12.8	1.15	↓
	13.8	.58*	0.1*
	15.9	1.75	.16
	16.1	1.64*	.22*
	17.0	1.81	.05
	17.0	1.66*	.1*
	19.7	1.34	.04
	22.0	1.37	.04
	22.0	1.08	.03
	22.0	.66*	0.1*
A26	3.5	1.59	.03
	5.5	1.54	.03
	7.9	1.60	.03
	11.0	1.50	.03
	11.8	1.60	.03
	14.1	1.45	.03
	16.8	1.58	.03
	18.7	1.60	.04
	20.1	1.48	.16
	21.5	1.61	.06
	21.5	1.10*	.05*
A27	2.4	1.70	.03
	4.8	1.60	.04
	6.5	1.58	.04
	8.7	1.58	.03
	11.8	1.66	.03
	14.0	1.66	.03
	18.4	1.66	.03
	20.5	1.10*	0.1*
	20.8	1.84	.10
A28	2.1	1.68	.03
	4.3	1.54	.03
	6.8	1.60	.03
	8.7	1.59	
A29	2.3	1.70	.03
	4.3	1.63	.03
	6.9	1.68	.03
A30	3.8	1.64	.03
	5.7	1.58	↓
	7.8	1.60	↓
	10.4	1.60	↓
	12.7	1.58	↓
A30A	2.0	1.66	.03
	3.6	1.46	.10
A32	2.0	.08	.04
	5.1	.80	.03
	7.4	.03	.03
	10.7	.83	.18
	10.7	.02*	.11*
A33	1.5	.81	.03
	3.8	.88	.03
	6.5	.84	.03
	8.1	.87	.03
	11.5	.58	.03
	11.5	.07*	< .03*

* Based on gas chromatograph analysis. Other numbers are via ultraviolet absorption.

TABLE B-4. (Cont'd.)

H_2S Content of Off Gas from Cycling Runs Dry Basis

Run No.	Cycle No.	Mol % H_2S from Regenerator	Mol % H_2S from Gas Desulfurizer, & COS
A35	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
A36	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	-
	[illegible]	[illegible]	-
	[illegible]	[illegible]	-
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
A36A	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	-
	[illegible]	[illegible]	[illegible]
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
A37	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	-
	[illegible]	[illegible]	-
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
A38	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
	[illegible] + [illegible] min.	[illegible]	-
A41	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
A42	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	ca. [illegible]*	[illegible]
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	

* Based on gas chromatograph analysis. Other numbers are via ultraviolet absorption.

TABLE D-5 (Cont'd.)

H_2S Content of Exit Gas from Cycling Runs
Dry Basis

Run No.	Cycle No.	Mol % H_2S from Regenerator	Mol % H_2S from Gas Desulfurizer, ± .01%
A43	0.5	1.30	.03
	1.5	1.38	.03
	3.0	1.38	ca. .04
	5.5	1.33	-
	7.5	1.66	ca. .04
	9.0	1.31*	-
	10.1	1.30	-
	12.0	1.30	.03
	14.3	--	.08*
	15.3	1.70	.18
	16.2	1.46*	-
A44A	1.5	1.33	.03
	3.0	1.56	.03
	5.0	1.34	.03
	6.5	1.46	.03
	7.5	1.36*	.02*
	9.0	1.38	.03
	10.0	1.58	.06
	11.4	--	.16*
	11.5	1.36	.20
	11.5 + 15 min.	.96	
	11.5 + 30 min.	.68	
	11.5 + 45 min.	.60	
	11.5 + 60 min.	.41	
	11.5 + 120 min.	.38	
	11.5 + 180 min.	.30	
	11.5 + 240 min.	.24	
A45	0.5	.78	.04
	1.7	.84	.04
	3.7	.84	.03
	6.0	.80	.03
	7.4	.93	.03
	9.0	1.06	.03
	12.6	1.24	.10
	13.5	1.30*	.08*
	15.5	1.24	.18
	15.5 + 15 min.	.94	
	15.5 + 30 min.	.83	
	15.5 + 45 min.	.78	
	15.5 + 60 min.	.56	
	15.5 + 120 min.	.30	
	15.5 + 180 min.	.10	
A46	3.0	.83	.03
	5.1	.88	.03
	8.1	.80	.03
	10.9	.95	.04
	13.0	1.13	.10
	17.1	.76	.03
	19.7	.76	.03
	23.3	.81	.03
	24.8	.52*	.02*
	26.7	.75	.03
	30.4	.80	.04
	33.6	.80	.03
	36.4	.59*	.01*
	37.0	.80	.04
	40.0	.80	.04

* Based on gas chromatograph analysis. Other numbers are via ultraviolet absorption.

TABLE [illegible] (Cont'd.)

H_2S Content of Exit Gas from Cycling Runs
Dry Basis

Run No.	Cycle No.	Mol % H_2S from Regenerator	Mol % H_2S from Gas Desulfurizer, [illegible]
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible](1)	[illegible]	[illegible]
	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]	[illegible]	
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
	[illegible] + [illegible] min.	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]*	[illegible]*
	[illegible]	[illegible]	[illegible]

(1) Adjusted H_2S analyzer.

* Based on gas chromatograph analysis. Other numbers are via ultraviolet absorption.

TABLE B-3

Attrition Data

Run No.	Cycle Number Start	Cycle Number End	Attrition, % of Feed Rate
A19	0	6.0	1.39
	6.0	11.9	.86
	11.9	17.7	.88
A20A	0	7.1	.73
	7.1	10.9	.91
	13.5	17.6	.74
	17.6	20.6	.81
	20.6	31.8	.84
A21	0	3.4	.74
	3.4	6.7	.76
	6.7	11.3	.98
	11.3	17.3	.79
	17.3	23.8	.93
	23.8	30.0	1.05
	30.0	36.9	.88
A22A	0	0.9	.57
	0.9	6.4	.56
	6.4	12.9	.58
	12.9	15.6	.87
	15.6	22.3	.81
A23	0	1.7	.79
	1.7	4.5	.81
	4.5	9.1	.80
	9.1	15.3	.86
	15.3	22.9	.84
A24	0	5.2	.75
	5.2	15.7	.79
A25	0	3.1	.82
	3.1	10.1	.80
	10.1	21.1	.76
	21.1	28.0	.76
	28.0	36.1	.71
A26	0	8.5	.81
	8.5	12.8	.59
	12.8	21.7	.85
A27	0	6.4	.89
	6.4	13.0	.74
	13.0	20.7	.79
A28	0	9.8	.68
A29	0	2.3	1.14
	2.3	4.5	.78
	4.5	7.3	.86
A30	0	1.0	2.27
	1.0	3.5	1.60
	3.5	7.6	1.24
	7.6	12.8	1.04
A30A	0.9	3.7	2.01

TABLE B-3 - Cont'd.

Attrition Data

Run No.	Cycle Number Start	Cycle Number End	Attrition, % of Feed Rate
A32	0.0	5.0	1.70
	5.0	11.0	1.85
A33	0.0	2.9	1.70
	2.9	5.9	2.66
	5.9	8.6	3.41
	8.6	11.6	3.43
A35	0.0	3.6	.95
	3.6	6.1	.70
	6.1	13.6	.58
A36	0	3.7	1.96
	3.7	6.6	1.45
A36A	0.0	5.5	1.62
	5.5	9.7	1.53
	9.7	14.3	1.24
	14.3	20.0	1.16
A37	0	6.9	.87
	6.9	9.3	.53
A38	0	3.5	.66
	3.5	7.4	1.13
	7.4	12.0	.90
A41	0	5.4	.34
A42	0	3.3	2.10
	3.3	4.7	2.25
	4.7	9.9	1.26
A43	0	4.2	1.52
	4.2	7.9	2.01
	7.9	11.4	2.11
A44A	0	2.5	.67
	2.5	6.5	.87
	6.5	9.0	1.22
	9.0	11.7	.67
A45	0	2.8	2.10
	2.8	6.3	1.45
	6.3	10.1	1.33
	10.1	15.6	.99
A46	0	2.1	1.08
	2.1	4.4	1.12
	4.4	8.1	1.04
	8.1	12.9	.90
	12.9	20.1	.70
	20.1	25.6	.47
	25.6	33.7	.44
	33.7	48.5	.40

TABLE B-2 - Cont'd.

Attrition Data

Run No.	Cycle Number Start	Cycle Number End	Attrition, % of Feed Rate
A47	0	4.8	.89
	4.8	8.3	.96
	8.3	12.0	1.03
	12.0	16.3	1.08
	16.3	22.6	.83
	22.6	27.7	.61
	27.7	33.8	.64
	33.8	40.3	.52
	40.3	48.3	.48
	48.3	58.1	.46
A48	1.0	5.8	.47
	5.8	15.0	.10
	15.0	19.9	.26
	19.9	24.3	.29
A51	0	4.6	.44
	4.6	9.8	.64
	9.8	14.1	.64
A53A	1.3	7.0	.72
	7.0	15.3	.91
	15.3	20.9	1.20
	20.9	26.7	.87
	26.7	33.5	.87
	33.5	36.7	.88

TABLE B-4

H_2S Content of Exit Gas - Batch Variable Studies

Dry Basis

Run No.	Time, Min.	Mol % H_2S	Run No.	Time, Min.	Mol % H_2S
A68	8	1.77	A69	5	2.38
	14	1.53		9	2.76
	24	1.19		15	2.54
	41	.99		24	2.07
	71	.67		39	1.66
	101	.58		54	1.33
	129	.52		84	.88
	159	.40		114	.60
	189	.34		144	.40
	249	.28		174	.29
	309	.20		234	.18
	369	.17		294	.09
	429	.10		354	.07
				414	.05
				474	.03
A70	9	2.86	A71	8	.27
	19	2.68		23	.36
	29	2.45		30	.41
	45	2.01		44	.41
	59	1.61		53	.38
	75	1.16		68	.37
	90	.84		83	.23
	105	.58		113	.17
	120	.42		143	.14
	150	.25		173	.13
	180	.14		233	.11
	240	.05		293	.08
	300	.04		353	.08
	344	.03		413	.06
				473	.06
A72	8	.61	A73	7	.89
	15	.79		13	1.40
	30	.77		18	1.43
	45	.65		28	1.43
	60	.51		43	1.13
	75	.44		58	.72
	90	.37		73	.50
	120	.24		88	.35
	150	.20		118	.22
	180	.17		148	.14
	210	.13		178	.08
	240	.10		238	.05
	285	.08		298	.02
	345	.06			
	405	.04			
	465	.04			

TABLE D-4 - Cont'd.

H_2S Content of Exit Gas - Batch Variable Studies

Dry Basis

Run No.	Time, Min.	Mol % H_2S	Run No.	Time, Min.	Mol % H_2S
A74	1	.32	A75	5	.64
	5	.28		8	.63
	11	.23		18	.53
	17	.20		25	.48
	29	.19		40	.34
	47	.15		55	.28
	77	.11		70	.30
	107	.10		85	.23
	167	.08		115	.21
	227	.06		145	.20
	287	.06		205	.16
	347	.05		265	.12
	407	.04		325	.10
	467	.05		385	.09
				445	.09
				505	.08
A76	3	.66	A77	3	.063
	5	.67		7	.093
	7	.80		25	.080
	13	.62		38	.057
	23	.65		50	.048
	33	.60		68	.044
	43	.54		93	.033
	58	.48		123	.031
	73	.44		153	.029
	88	.41		183	.025
	103	.38		213	.023
	133	.33			
	163	.31			
	193	.27			
	223	.26			
	283	.22			
	343	.19			
	403	.16			
	463	.14			

TABLE B-1 - Cont'd.

H_2S Content of Exit Gas - Batch Variable Studies
Dry Basis

Run No.	Time, Min.	Mol % H_2S	Run No.	Time, Min.	Mol % H_2S
A78	4	.17	A79	3	.35
	9	.195		7	.39
	12	.19		10	.37
	24	.14		20	.28
	33	.13		27	.25
	48	.10		32	.23
	63	.09		47	.19
	93	.07		62	.17
	123	.06		77	.15
	153	.05		107	.13
	183	.05		137	.11
	243	.04		197	.10
	303	.04		257	.08
	363	.03		317	.07
	423	.03		377	.07
	468	.03		437	.06
				477	.05
A80	1	.17	A81	7	.33
	5	.25		9	.39
	14	.31		12	.44
	29	.29		15	.47
	44	.28		22	.46
	74	.23		37	.45
	104	.20		55	.42
	134	.20		82	.36
	164	.17		112	.31
	194	.14		172	.22
	224	.13		232	.14
	284	.10		292	.08
	344	.08		352	.05
	404	.07		412	.03
	464	.06		472	.03

APPENDIX C

Thermodynamic Data

Introduction

Thermodynamic data for equilibrium and heat balance calculations pertinent to the hot sulfur removal process were published previously.(1) These data are included here again for convenience to the reader.

Source of Data

A. Gaseous Phase

Nearly all of the standard free energy of formation values, heat capacities at zero pressure, and the standard heats of formation were taken from the JANAF Thermochemical Tables.([illegible]) Exceptions in the sources of data were:

1. The heat capacity and heat of formation for $S_6(g)$ were calculated from the JANAF tables for $S_8(g)$ and the experimental data in the equilibrium constants measured experimentally by Preuner and Schupp.([illegible])

2. The vapor pressure and heat of vaporization of liquid sulfur were taken from West.([illegible])

3. The heat content of steam above liquid water were values given in the Keenan and Keyes steam tables.

B. Solid Phase

Sources of data involving calcium compounds are primarily experimental equilibrium measurements which were supported privately by CCDC during the 1960's. CCDC([illegible]) published equilibrium constant data in the reactions:

$$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2 \qquad (1)$$

$$CaO + H_2S = CaS + H_2O \qquad (2)$$

and

$$CaCO_3 = CaO + CO_2 \qquad (3)$$

The results were in agreement and extended the prior experimental measurements of the above reactions.([illegible])

The reaction,

$$CaCO_3 + H_2S = CaS + CO_2 + H_2O \qquad (4)$$

by which gas desulfurizing and acceptor regeneration occurs is the sum of reactions (2) and (3) above.

Preceding page blank

For reactions involving solids, we prefer to use experimentally determined values of the equilibrium constants in order to avoid the errors involved in: 1) the use of the sometimes uncertain or discordant free energy values in the literature, and 2) the extrapolation of free energy data to temperatures of interest to the process.

Equilibria in many reactions for which we have no experimental data can be calculated accurately by summing one or more of the reactions (1), (2), and (3) above, with gaseous reactions for which the free energies are well-established. For example, consider the reaction,

$$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$$

This reaction can be expressed as the sum of the following reactions:

	Equilibrium Constant
$CaO + H_2S = CaS + H_2O$	K18
$H_2O + 1/4\ S_2 = H_2 + 1/2\ SO_2$	$(1/K5)^{1/2}$
$H_2 + 1/2\ S_2 = H_2S$	K8
$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$	K19

Thus,

$$K19 = \frac{(K18)(K8)}{(K5)^{1/2}}$$

The above equilibrium constants are those identified in Tables C-2 and C-7.

Presentation of Data

Distribution of sulfur vapor species are presented in Table C-1.

Equilibrium constants for gas reactions are shown in Table C-2 and numerical values of the constants as a function of temperature are in Table C-3. Heat capacities are in Table C-4 and the mean heat capacities above 60°F, derived from Table C-4 data, are in Table C-5. The heat content of steam above liquid water at 60°F also is given in Table C-5.

Heats of formation and heats of reaction at 60°F are given in Table C-6. Equations for the vapor pressure of liquid sulfur are shown in Figure C-1, which is a plot of the equations. An equation for the heat of vaporization of liquid sulfur also is given in Table C-6.

Equilibria for the pertinent solids reactions involving calcium compounds are given in Table C-7. Mean heat capacities above 60°F are shown in Table C-8. Heats of formation and heats of reaction are shown in Table C-9.

Plots of the equilibrium constants versus temperature for reactions involving CaS are shown in Figures C-2 and C-3.

[illegible]

Effect of Temperature and Sulfur Partial Pressure on Distribution of Sulfur Species

Mol Fraction			Partial Pressure of Total Sulfur, atm	Atoms Sulfur/Mol Total Sulfur
X_2	X_6	X_8		
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE C-2

Equilibrium Constants for Gas Reactions

Temperature in °Kelvin

$$\ln K = A + BT + CT^2 + D/T$$

	A	B	C x 10⁶	D	Temperature Range, °K
81 $CO + 1/2\ S_2 = COS$	−13.5985	.0025854	−8.03040	13,017.2	300-900
	−10.3503	.0008002	−.18812	11,287.0	900-1400
82 $H_2 + 1/2\ S_2 = H_2S$	−5.3740	−.0007184	1.01362	10,029.6	300-900
	−4.5823	−.0007315	.18766	10,480.5	900-1400
83 $2H_2 + SO_2 = 1/2\ S_2 + 2H_2O$	−4.8009	.0002870	−2.26137	15,233.9	300-900
	−1.4871	−.0001610	.42850	14,786.0	900-1400
84 $2CO + SO_2 = 1/2\ S_2 + 2CO_2$	−15.7362	.0050024	−2.65407	25,277.0	300-900
	−14.3340	.0015907	−.35856	25,314.0	900-1400
85 $3S_8 = 4S_6$	21.5713	−.000282	3.3025	−15,135.4	300-900
86 $S_8 = 4S_2$	−22.2782	.120224	−63.5707	−29,296.0	300-600
88 $2H_2S + SO_2 = 3/2\ S_2 + 2H_2O$	1.89482	.0004522	−4.0404	−4871.84	300-900
87 $H_2O + CO = H_2 + CO_2$	−4.21477	.0016983	−.34481	5,187.25	900-1400
89 $CO + 3H_2 = CH_4 + H_2O$	−31.415	.0009854	−1.05181	28,104	900-1200

TABLE C-3

Numerical Values of Equilibrium Constants for Table C-2

Temperature in °F

°F	K1	K2	K3	K4	K5	K6	K7	K8	K9
200	1.25×10^{9}	1.55×10^{10}	1.80×10^{16}	5.27×10^{23}	3.17×10^{-9}	2.03×10^{-40}	.000748		
300	1.66×10^{7}	2.76×10^{8}	1.45×10^{14}	8.45×10^{19}	3.80×10^{-7}	2.61×10^{-28}	.00190		
400	8.04×10^{5}	1.57×10^{7}	2.26×10^{12}	3.35×10^{16}	2.46×10^{-5}	5.75×10^{-22}	.00914		
500	73,900	1.60×10^{6}	8.36×10^{10}	4.25×10^{14}	6.63×10^{-4}	1.56×10^{-16}	.0225	-	
600	10,800	2.49×10^{5}	5.72×10^{9}	5.62×10^{12}	9.81×10^{-3}	6.46×10^{-13}	.0825	-	
700	2,050	5.27×10^{4}	6.75×10^{8}	1.55×10^{11}	.0837	1.26×10^{-9}	.221	-	
800	505	1.42×10^{4}	9.25×10^{7}	7.55×10^{9}	.646	6.30×10^{-7}	.461	-	
900	158	4,520	1.82×10^{7}	5.73×10^{8}	3.40	1.25×10^{-4}	.856	-	-
1000	54.1	1,720	4.38×10^{6}	6.18×10^{7}	15.1	.0209	1.44	-	-
1200	11.4	353	4.01×10^{5}	1.55×10^{6}	188	9.54	3.22	1.965	6.97×10^{-7}
1400	3.18	98.6	6.35×10^{4}	9.15×10^{4}	—		6.39	1.20	1.589×10^{-7}
1600	1.15	35.9	1.38×10^{4}	9,280	—		10.7	.819	1.224×10^{-8}
1800	.501	15.5	3,500	1,480	—		16.2	.603	1.486×10^{-8}
2000	.251	7.64	1,340	296	—		22.5	.471	-

TABLE C-4

Heat Capacities at Zero Pressure

Temperature in °Kelvin

$$C_p = A + BT + CT^2 + DT^3 + E/T^2$$

	A	B	C x 10⁶	D x 10⁹	E	Temp. Range, °K
S_8	26.51	.03771	-25.25			300-800
S_6	33.13	.01863	-8.137			300-1000
S_2	8.633	.000272			-87,856	300-1400
COS	9.678	.003678	-.1003		-153,858	
H_2S	7.344	.001821	3.364	-1.093		
SO_2	6.085	.01334	-11.003	2.848		
N_2	7.098	-.001431	3.400	-1.348		
CO	6.551	.003185	-.8609		48,814	
CO_2	6.101	.015608	-10.238	2.552		
H_2	7.019	-.000874	.0840		-16,008	
$H_2O(g)$	7.787	.0000005	3.219	-1.135		
CH_4	1.0800	.021486	-5.80317		112,176	
O_2	6.085	.0036381	-1.0200	.2025		
Air	6.8864	.002072	-.53307		38,076	300-1000

TABLE C-5

Mean Heat Capacities Above 60°F, Gases

Temperatures in °F

$$\bar{C}_p = A + BT + CT^2 + DT^3$$

Btu/Lb Mol/°F

	A	B	C x 10⁶	D x 10⁹	Temp. Range, °F
[illegible]	36.003	.006734	-2.590		60-1000
[illegible]	17.940	.004076	-.331		60-1500
S_2	7.680	.001541	-.640	.126	60-2000
COS	9.718	.003033	-1.096	.177	
H_2S	8.005	.000016	.914	-.070	
SO_2	9.274	.003706	-.858	.181	
N_2	6.941	.000137	.255	-.058	
CO	6.925	.000105	.266	-.076	
CO_2	8.533	.003658	-.844	.109	
H_2	6.910	.000135	-.044	.082	
$H_2O_{(g)}$	7.974	.000410	.339	-.048	
CH_4	8.1918	.0035301	.4734	-.5313	
O_2	6.9211	.00077633	-.1449	.019082	
Air	6.853	-.000003471	.3639	-.1108	60-1240

Heat content of steam (1 atm) above liquid water at 60°F.

Btu/Lb = 1021.08 + .45340T - 35.83 x 10^{-6} T^2 + 34.48 x 10^{-9} T^3 220-1000

Btu/Lb = 1039.25 + .41010T + 40.00 x 10^{-6} T^2 1000-1800*

---

* Can be extrapolated accurately to 2000°F.

TABLE C-6

Heats of Formation at 25°C, Gases

cal/g mol

	ΔHf
$S_{8(g)}$	+24,200
$S_{6(g)}$	+25,580
$S_{2(g)}$	+30,840
COS	-33,080
H_2S	-4,880
SO_2	-70,960
CO	-26,416
CO_2	-94,052
$H_2O_{(g)}$	-57,798
$H_2O_{(l)}$	-68,317
CH_4	-17,889

Heats of Reaction at 25°C, Gas Reactions

cal/g mol

Reaction		
1	$CO + 1/2\ S_2 = COS$	-22,080
2	$H_2 + 1/2\ S_2 = H_2S$	-20,300
3	$2H_2 + SO_2 = 1/2\ S_2 + 2H_2O_{(g)}$	-29,220
4	$2CO + SO_2 = 1/2\ S_2 + 2CO_2$	-48,890
5	$2H_2S + SO_2 = 3/2\ S_2 + 2H_2O_{(g)}$	+11,380
6	$3S_8 = 4S_6$	+29,720
7	$S_8 = 4S_2$	+99,160
6a	$1/6\ S_6 = 1/2\ S_2$	+11,160
7a	$1/8\ S_8 = 1/2\ S_2$	+12,400
5a	$2H_2S + SO_2 = 1/2\ S_6 + 2H_2O_{(g)}$	-22,090
5b	$2H_2S + SO_2 = 3/8\ S_8 + 2H_2O_{(g)}$	-25,800

Heat of Vaporization of Sulfur

Temperature in °F

$$Btu/lb = 211.1 - .3308T + 436.8 \times 10^{-6}\ T^2 - 214.4 \times 10^{-9}\ T^3$$

TABLE C-7

Equilibrium Constants for Solids Reactions

Temperature in °Fahrenheit

$\ln K = A + BT + CT^2 + D/T$

		A	B	C x 10⁶	D	Temperature Range, °F
K10	$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2$	71.5076	-.102350	3.79855	-47,104	1500-2000
K11	$1/4\ CaSO_4 + CO = 1/4\ CaS + CO_2$	3.0040	-.000751	.01932	4,222	1500-3000
K12	$CaO + H_2S = CaS + H_2O$	17.5646	-.0050806	1.7726	-1,070	1300-2000
K13	$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$	-7.22273	.0055330	-.34880	15,250	1500-3000
K14	$CaSO_4 + S_2 = CaS + 2\ SO_2$	-6.55015	.0218712	-1.86065	-12,576	1500-2000
K15	$CaCO_3 = CaO + CO_2$	-.340165	.0074015	-1.28040	-12,922	all
K16	$CaCO_3 + H_2S = CaS + CO_2 + H_2O$	16.6790	-.0018225	.480212	-13,377.2	1100-2000

TABLE C-8

Mean Heat Capacities Above 60°F, Solids

Temperature in °Farenheit

$$\bar{C}p = A + BT + CT^2$$

Btu/lb Mol/°F

	A	B	C x 10⁶	Temperature Range, °F
$CaSO_4$	23.57	.00045	-.0383	60-2000
CaS	10.14	.00230	-.502	
CaO	10.98	.00071	-.0779	
MgO	9.77	.00081	-.0387	
MgO·CaO	20.75	.00152	-.116	
$MgO·CaCO_3$	20.64	.00560	-.103	
Char Carbon	1.447	.00291	-.649	
MgO·CaS	19.91	.00311	-.541	↓ (33,34)
		Btu/lb/°F		
Ash*	.207	.000050	-.0034	60-2000(34)
		Heat Content Above 60°F Btu/lb		
Coal**	-13.9	.1879	.253	60-950

* Also used for impurity content of acceptor.

** Including products of pyrolysis.

TABLE C-9

Heats of Formation at 25°C, Solids

cal/g mol

	ΔH_f
$CaSO_4$	-344,090
CaS	-112,550
$CaCO_3$	-288,280
CaO	-151,900

Heats of Reaction at 25°C, Solids Reactions

cal/g mol

$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2$	+63,600
$1/4\ CaSO_4 + CO = 1/4\ CaS + CO_2$	-10,008
$CaO + H_2S = CaS + H_2O_{(g)}$	-14,870
$CaO + 3/4\ S_2 = CaS + 1/2\ SO_2$	-20,580
$CaSO_4 + S_2 = CaS + 2\ SO_2$	+57,780
$CaCO_3 = CaO + CO_2$	+42,330
$CaCO_3 + H_2S = CaS + CO_2 + H_2O_{(g)}$	+27,750
$CaS + 3/2\ O_2 = CaO + SO_2$	-109,810
$CaS + 2\ O_2 = CaSO_4$	-231,540

Heat of Combustion

Btu/lb mol

Char Carbon	178,540-4T*	(11)

---

* T is maximum temperature to which the char has been exposed, °Farenheit.

FIGURE C-1

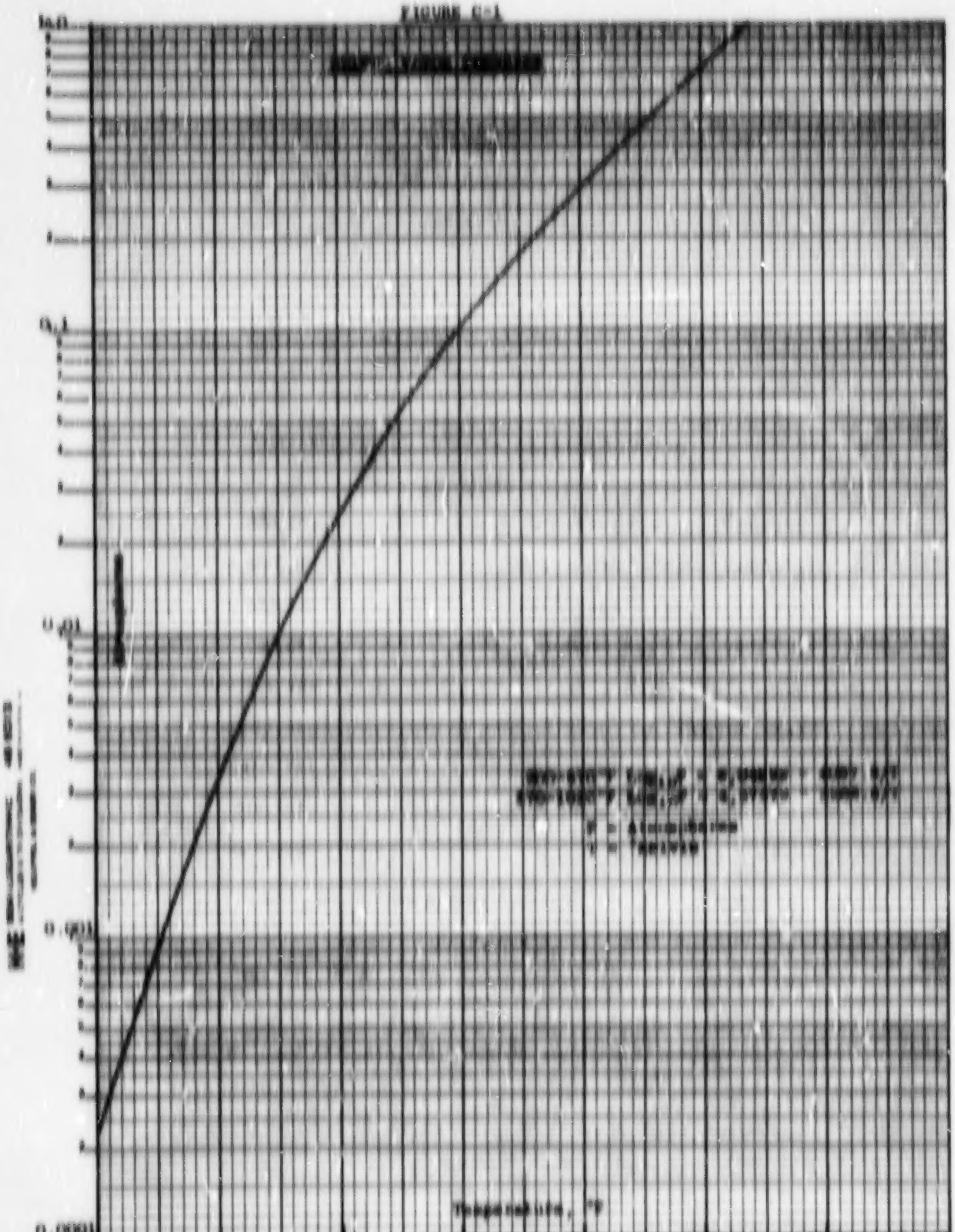
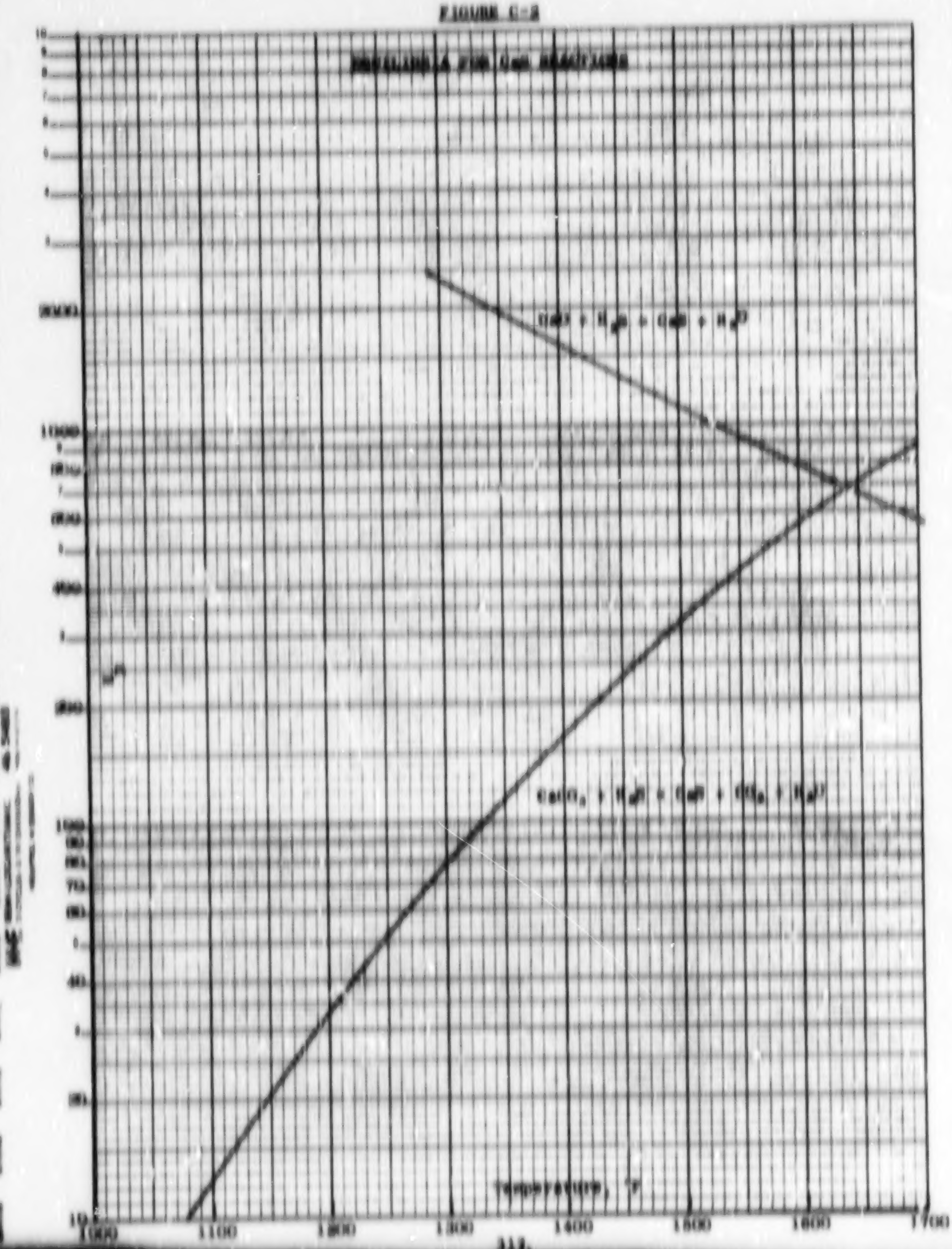
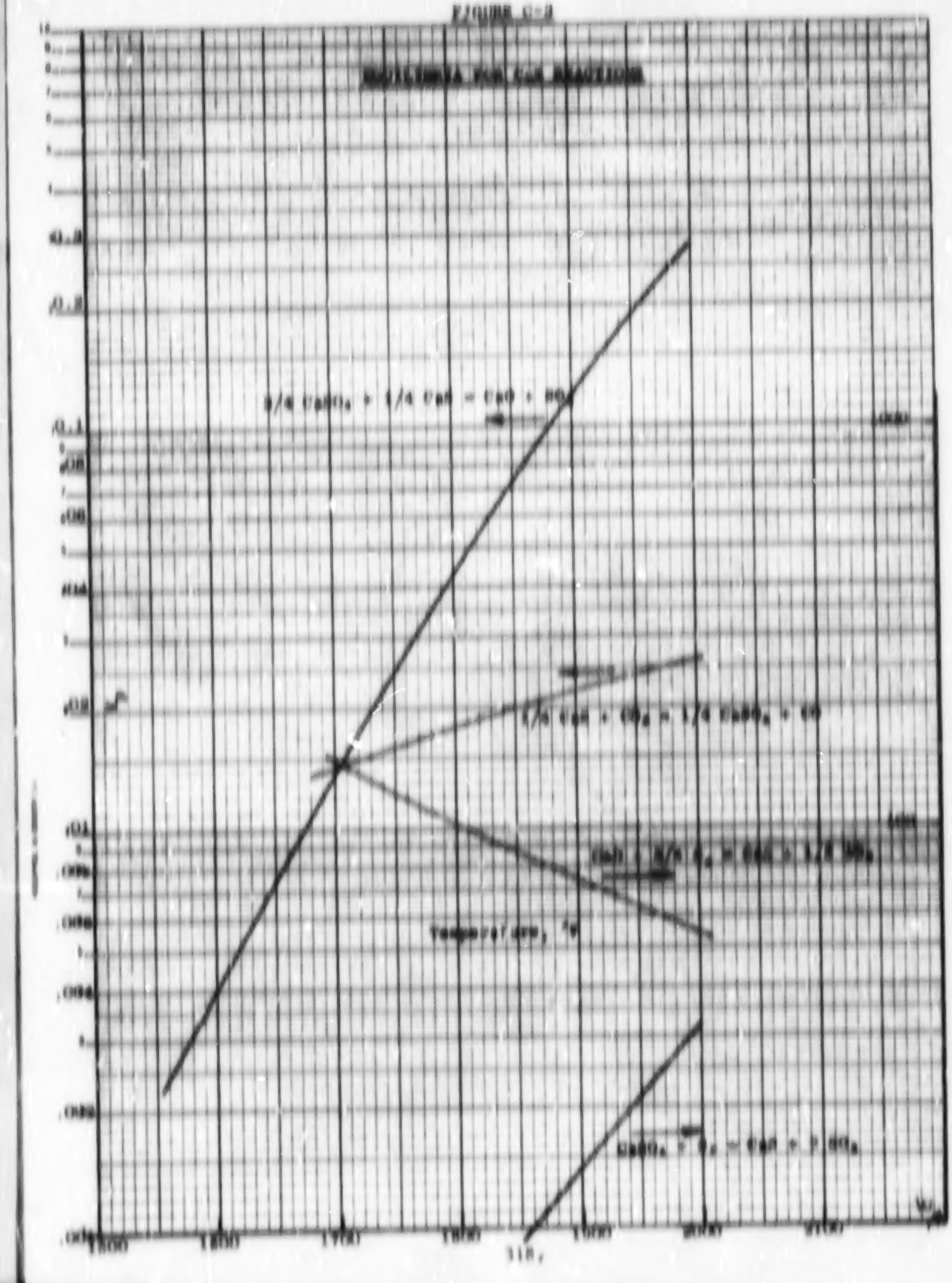


FIGURE C-2


EQUILIBRIA FOR CaS REACTIONS
10000
1000
100
10
$CaS + H_2O = CaO + H_2S$
$CaCO_3 + H_2S = CaS + CO_2 + H_2O$
Temperature, °F
1000
1100
1200
1300
1400
1500
1600
1700


0.3
0.2
3/4 CaSO₄ + 1/4 CaS = CaO + SO₂
0.1
.08
.06
.04
.02
1/4 CaS + CO₂ = 1/4 CaSO₄ + CO
.01
.008
.006
Temperature, °F
.004
.002
.001
1500
1600
1700
1800
1900
2000
2100

APPENDIX D

Comparison of CCDC Process to Hot Carbonate Scrubbing

In 1973 there was a mutual agreement to expand the Scope of Work under this contract to include an economic comparison between the CCDC (then Consol) hot gas cleanup process and a conventional gas desulfurization process. The study was completed in November, 1973, issued as Consolidation Coal Research Memorandum RM-13461, submitted to EPA on November 30, 1973, and is enclosed here.

The study compared the cost of the Consol (now CCDC) hot gas cleanup process to the cost of wet scrubbing and gas desulfurization by the hot carbonate process. The cost of desulfurization by the Consol process was about 30% less (see Table I, page 4 of the enclosed memorandum).

CONSOLIDATION COAL COMPANY

Research Division

Library, Pennsylvania

November 20, 1973

MEMORANDUM - RM-13451

To : J. A. Phinney

From : G. D. Rutledge and J. T. Clancey

Subject: Cost of Pressurized Producer Gas Desulfurization

I. Introduction

The scope of work under EPA Contract No. 68-02-1333 requires an economic comparison of two methods of producer gas desulfurization. This was done by developing the cost of conventional, low-temperature desulfurization technology for comparison with that of the lime-based hot gas desulfurization system being developed under the above EPA contract.

Briefly, the hot process desulfurizes pressurized gasifier gas at about 1650°F in a fluidized bed of a regenerative, lime-based sulfur acceptor. The desulfurized producer gas is cleaned of particulates and alkali by high pressure drop cyclones and then is cooled to 1300°F by heat exchange with the water needed to generate the gasifier steam. The sulfided acceptor is conveyed to the regenerator in a stream of CO_2 and steam, where sulfur is evolved as H_2S at 1300°F. The regenerated acceptor is returned by gravity to the desulfurizer. The H_2S in the regenerator offgas is converted to elemental sulfur with dilute aqueous H_2SO_3 in the liquid-phase Claus reaction. Unreacted gas is recirculated to the regenerator. The spent aqueous H_2SO_3 is then reconcentrated in a packed column by absorbing SO_2. The SO_2 is generated from burning one-third of the sulfur produced.

The Annual Report(1) under EPA Contract No. EHSD-71-15 details the system under study and also gives an economic analysis of its cost. Two methods of particulate and alkali removal were covered in that study; hot removal only in high pressure drop cyclones and wet removal with water in Venturi scrubbers. The description and the economic analysis for the hot particulate removal method is used in this study as the basis for evaluation.

In the conventional desulfurization process, the hot gasifier gas must be cooled by heat exchange and wet scrubbing. The gas then can be desulfurized by contact with one of the commercially available chemical or physical liquid absorbents. To recover heat from the hot gas, the cool desulfurized gas is reheated to about 1290°F. Absorbed H_2S is stripped from the liquid absorbent and converted to elemental sulfur in the standard Claus reaction. The high sulfur content of the Claus tail gas also necessitates the inclusion of a tail gas clean up step. Depending upon the method selected, sulfur can be recovered directly as elemental sulfur or as a concentrated stream of either SO_2 or H_2S for recirculation to the Claus converters.

The hot potassium carbonate process was selected as the conventional method of sulfur removal. The selection was made primarily because the technology for design is available in the literature.(3,5,4,6) Although the basic hot potassium carbonate process is reported to be selective(6) for H_2S, there are no known commercial applications. Lack of published data on the selectivity prevents the evaluation of this design feature. The potential problem with hot potassium carbonate may be the inability to remove the non-acidic sulfur gases (COS, CS_2 and thiophene) formed in coal gasification. If these gases are formed in sufficient amounts, then one of the selective, physical solvents may be the only viable conventional desulfurization process.

To complete the conventional system, the direct oxidation Claus process was selected for sulfur recovery followed by the Wellman-Lord SO_2 recovery process for tail gas cleanup. The low H_2S concentration (about 6 volume %) in the acid gas feed necessitates the use of direct oxidation. The Wellman-Lord SO_2 recovery process was selected because low SO_2 effluent levels (<100 ppmv) in the stack gas have been achieved commercially.(7) These two conventional processes are comparable to the liquid-phase Claus used in the hot gas desulfurization system.

II. *Summary*

An economic evaluation of desulfurizing pressurized producer gas is required under this EPA contract. The purpose is to determine the potential economic incentive for further development and pilot plant work. The study is restricted to the cost of desulfurizing the producer gas. The cost of gasification is not included, nor are estimates developed for the cost of generating electric power from the desulfurized producer gas.

For the evaluation, the plant size was selected to supply a desulfurized fuel gas to a conventional, gas-burning power station with an approximate rating of 1400 MW. With respect to quantity of gas, this is the same size plant that was considered in the previous studies.

In the study, a conventional, low-temperature desulfurization system is evaluated and compared to the hot gas desulfurization system. The hot gas desulfurization system removes sulfur via regenerative acceptor and recovers sulfur via liquid-phase Claus. The conventional desulfurization system removes sulfur via hot potassium carbonate and recovers sulfur via direct oxidation Claus and Wellman-Lord SO_2 recovery.

The results of the study show a significant advantage is to be gained over conventional technology by the development of hot gas desulfurization. The advantage is about $3.50 per ton of feed coal, or 13.1¢/MM Btu of product gas. About one-half of the cost saving (5.3¢/MM Btu) would be gained from the development of a hot gas clean up technology for alkali and particulate removal to replace the conventional wet scrubbing and gas reheat. (Note: the last Annual Report[1] developed the cost of incorporating wet scrubbing and reheat into the hot gas desulfurization system. These costs, $4.98 per ton of feed coal and 25.4¢ per MM Btu (HHV + sensible heat) of product gas, can be compared with the desulfurization costs in Table IV, Section V.) The remainder of the advantage (7.8¢/MM Btu) is gained from the lower direct operating cost of the hot system. The higher operating cost of the conventional system is chiefly caused by the following: 1) the reboiler import steam and cooling water requirement of the hot potassium carbonate process, and 2) the fuel gas necessary to preheat the feed gas and incinerate the tail gas of the direct oxidation Claus process.

The evaluation results, based on an arbitrary start-up date of January, 1978, are summarized in Table I. In addition to the cost advantage shown in Table I for hot (Case I) over conventional desulfurization (Case II), there is also a greater amount of excess power available from expansion of the product gas (about 22 MW equivalent). While it is beyond the scope of this study to evaluate the dollar value of this excess power, it could amount to an additional credit of 0.5-0.6¢/MM Btu of product gas.

The cost of the plant facilities per installed KW (1973 cost basis) to desulfurize producer gas under pressure amounts to $33 for Case I versus $40 for Case II. The annual operating cost corresponds to 1.6 and 2.4 mills/KWh of power generated for Cases I and II, respectively.

The make-up acceptor cost for this evaluation was assumed at a relatively high value of $10 per ton of raw dolomite. The make-up acceptor requirement for the regenerative acceptor case is, however, quite modest, and the acceptor cost does not have a significant impact on the desulfurization cost. In this study, the rate of make-up acceptor required is estimated as one per cent of the circulating acceptor. This is based on a reasonable extrapolation of the laboratory data obtained to date. If the make-up rate were doubled, the desulfurization cost would increase only by 4-5%.

Interestingly, the sensible heat content of the desulfurized producer gas delivered to the power station is a significant factor. In a conventional, gas-fired power station, the fuel gas is delivered to the burners at ambient temperature. The combustion air is preheated to 550 to 650°F in an air heater by indirect sensible heat exchange with flue gas. In this process the fuel gas is delivered from the expander to the power station at 640-660°F. If the fuel gas is preheated, then either less air heater surface is required, or more steam can be generated per unit of fuel burned. An exact determination of the dollar value of sensible heat in the fuel gas would require an extensive analysis of the design and cost of the power station proper. This is beyond the scope of this study.

Table I

Summarized Economic Evaluation
70% Plant Operating Factor (6132 hrs/year)

Case	I	II
Method of Gas Desulfurization	Hot	Conventional
Desulfurization Process	Regenerative Acceptor	Hot Potassium Carbonate
Coal Required:		
MM Tons/Year (8% Moisture)	←— 2,422,000 —→	
Higher Heating Value, Btu/Year	←— 81.71×10^{12} —→	
Producer Gas to Station (After Expansion):		
Mols/Year	212,730	183,987
Temperature	860°F	650°F
Pressure	10 psig	10 psig
Higher Heating Value, Btu/Year	65.19×10^{12}	64.62×10^{12}
HHV + Sensible Heat Content,[1] Btu/Year	68.00×10^{12}	67.41×10^{12}
Desulfurization Plant Investment[2]	$48.3 MM	$88.8 MM
Desulfurization Cost:[2]		
$/Ton Feed Coal	4.22	6.58
¢/MM Btu HHV of Feed Coal	16.9	27.4
¢/MM Btu HHV of Product Gas	21.2	34.7
¢/MM Btu (HHV + Sensible Heat) Product Gas	20.1	33.2
Excess Power Generated by Expander, megawatts[3]	188[4]	185[4]

[1] Sensible heat content above an assumed air heater outlet temperature of 300°F.

[2] January, 1978 operation - Includes escalation and interest during construction. Does not include gasification plant cost or the cost of coal.

[3] After deduction of 157 MW required for compression of process air for gasification plant.

[4] Assuming 85% of the isentropic efficiency for the expander, and 80% of the polytropic efficiency for the air compressors.

GSR:mw

However, a reasonable approximation of the value is to credit the system for the sensible heat content of the fuel gas above the temperature of the flue gas exiting the air heater. In this study this temperature is assumed as 300°F. In Table I, the credit to the process for this excess sensible heat is about 1.0-1.5¢/MM Btu or about 5% of the system cost.

III. Recommendations and Conclusions

Based on the economic evaluation in this report, a significant advantage exists for hot gas desulfurization over conventional desulfurization. The magnitude of the advantage is sufficient incentive for further development and pilot plant work. Sufficient incentive exists for the hot gas desulfurization process even if wet scrubbing and reheat are ultimately necessary to produce adequate quality gas for an expander. This is because of the large energy requirement (import steam and fuel gas) of the conventional desulfurization process. The relative incentive for (1) hot sulfur acceptance (including wet scrubbing and reheat + liquid-phase Claus sulfur recovery) is $1.07 per ton of feed coal or 7.8¢/MM Btu (HHV + sen. heat) of product gas and (2) hot solids removal is $0.88 per ton of feed coal or 5.3¢/MM Btu of product gas.

IV. Process Description

A. General

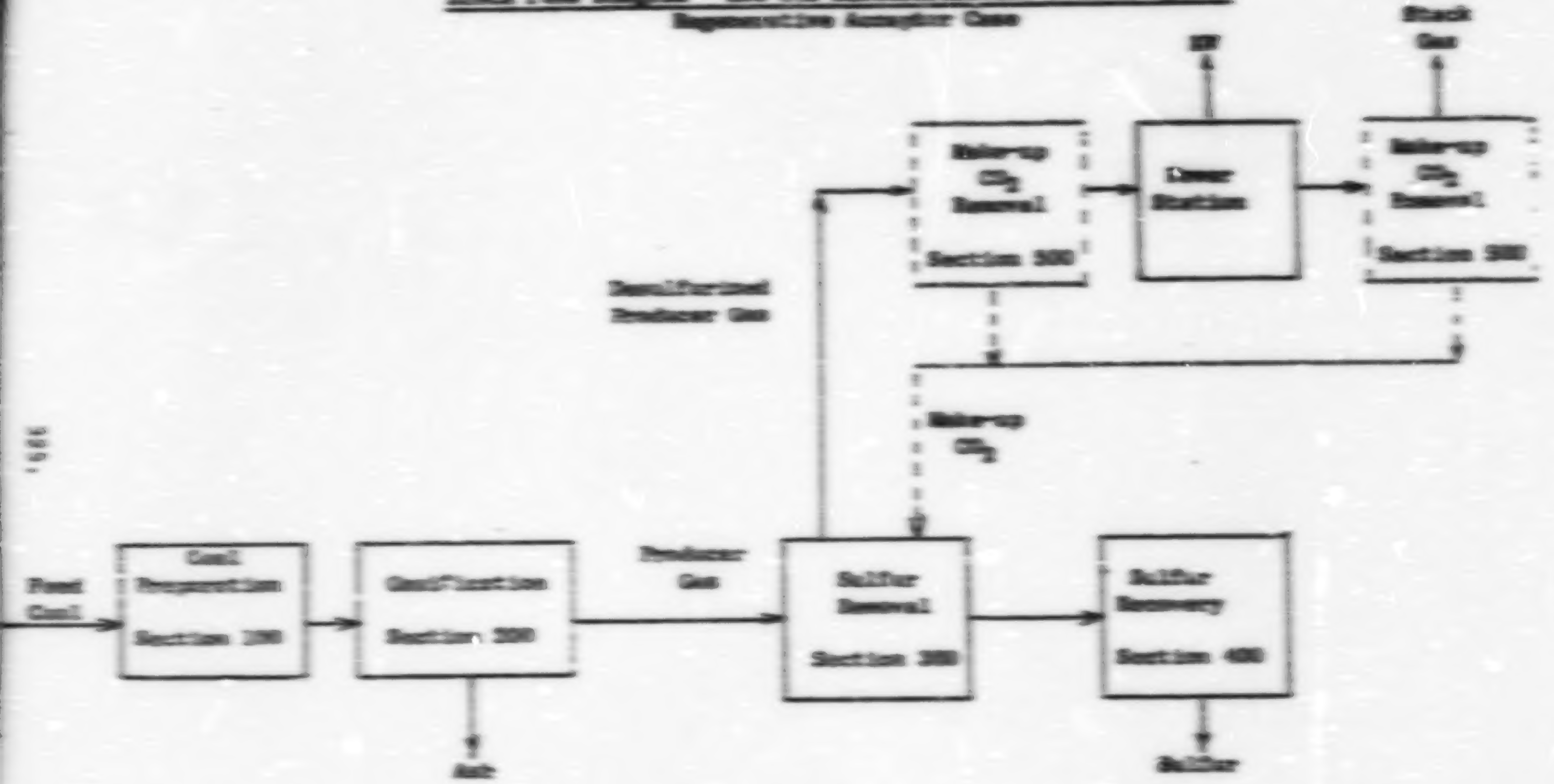
The simple block flow diagrams in Figure 1, hot gas desulfurization, and Figure 2, conventional gas desulfurization, define the steps in the overall process. The design and evaluation of coal preparation (crushing and sizing) and of coal gasification (Section 100 and 200, respectively), are not covered in this study.

In the hot gas desulfurization process, Section 300, sulfur removal by regenerative acceptor, and Section 400, sulfur recovery by liquid Claus, have been completely evaluated. A relatively small quantity of make-up CO_2 is required in the process (Section 500). As shown in Figure 1, the CO_2 could be recovered either from a slip-stream of the desulfurized producer gas before power generation, or from a portion of the power station stack gas. Preliminary cost studies indicate approximately equal costs for the two alternative locations. For the purposes of this study, it is assumed that the make-up CO_2 is recovered from the pressurized producer gas before delivery to the power station. A standard hot potassium carbonate system is assumed to establish capital cost and utility requirements.

In the conventional gas desulfurization process, Section 300, sulfur removal by hot potassium carbonate, Section 400, sulfur recovery by direct oxidation Claus, and Section 500, SO_2 recovery by Wellman-Lord process, have been evaluated. Section 600, wet scrubbing (particulate and alkali removal), and reheat has been evaluated as an integral part of the sulfur removal section.

Figure 1

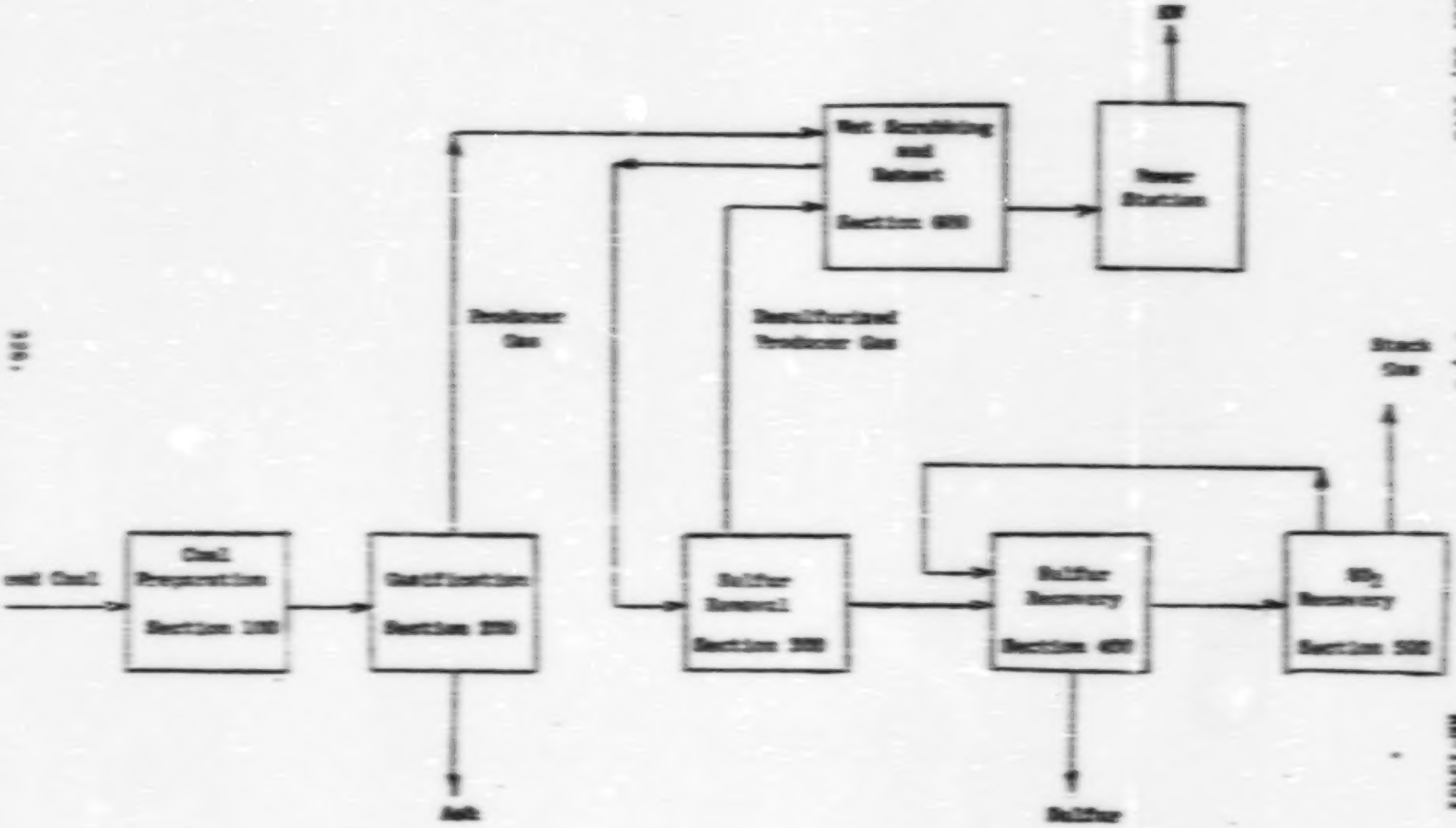
Block Flow Diagram - Hot Gas Desulfurization Overall System
Regenerative Acceptor Case


Stack Gas
HP
Makeup CO_2 Removal Section 500
Power Station
Makeup CO_2 Removal Section 500
Desulfurized Producer Gas
Makeup CO_2
Feed Coal
Coal Preparation Section 100
Gasification Section 200
Producer Gas
Sulfur Removal Section 300
Sulfur Recovery Section 400
Ash
Sulfur

Note: Alternative locations of Section 500 shown by dotted lines.

Figure 2

Block Flow Diagram - Conventional Gas Desulfurization Overall System
Hot Potassium Carbonate Case


aw Coal
Coal Preparation
Section 100
Gasification
Section 200
Ash
Producer Gas
Sulfur Removal
Section 300
Desulfurized Producer Gas
Hot Scrubbing and Reheat
Section 600
Power Station
KW
Sulfur Recovery
Section 400
Sulfur
SO_2 Recovery
Section 500
Stack Gas

B. Hot Gas Desulfurization

Sulfur Removal by Regenerative Acceptor

A schematic flow diagram of the proposed commercial embodiment of the hot gas desulfurization process is shown in Figure 3 (Consol Dwg. No. AF-8459).

Gasifier product gas (Stream No. 4) flows to the bottom of a fluidized gas desulfurizer (D-301). The gas fluidizes a bed of sized dolomite at a temperature of 1650°F and at 15 atm. absolute pressure. Most (97%) of the H_2S in the gasifier gas reacts with the $CaCO_3$ component of the dolomite as follows:

$$H_2S + MgO \cdot CaCO_3 = MgO \cdot CaS + CO_2 + H_2O$$

The desulfurized gasifier gas then passes through two stages of cyclones (G-301 and G-302, respectively), to remove substantially all of the entrained dolomite fines. A portion of the sensible heat content of the desulfurized gas is used to generate and superheat the steam required for gasification of the feed coal in heat exchangers C-302 and C-301, respectively. The desulfurized producer gas, at 1300°F and 210 psia (Stream No. 6), is then delivered to the power station. Subsequent use of this gas is dependent on the design of the power station, and is discussed later in this report.

Regenerated acceptor (Stream No. 5) at 1300°F is continuously charged to the top of the gas desulfurizer, and is continuously withdrawn via a standleg (Stream No. 7). The sulfided acceptor is pneumatically conveyed by a portion of the required recycle gas (Stream No. 9) to a fluidized acceptor regenerator (D-302). Make-up acceptor (Stream No. 8) is introduced into the system by a lockhopper system comprised of L-301, F-301, F-302, and L-302. This small stream is also pneumatically conveyed to D-302 by means of recycle gas. Make-up CO_2 required in D-302 (Stream No. 10) is pressurized by JC-301 and charged to D-302.

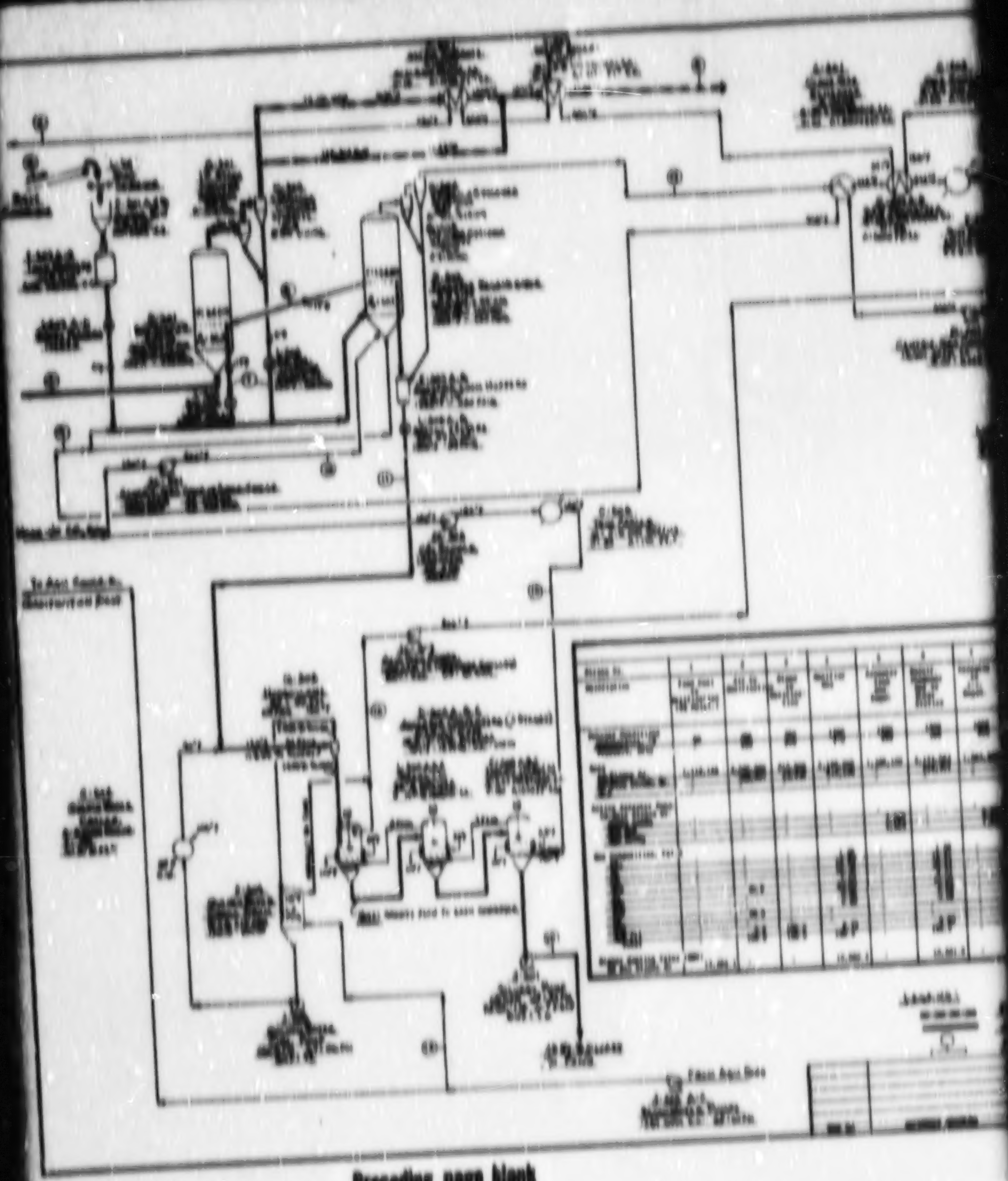
The fluidized acceptor regenerator (D-302) is maintained at 1300°F and 15 atm. absolute pressure. The sulfided acceptor is recarbonated at these conditions by the reverse reaction:

$$MgO \cdot CaS + CO_2 + H_2O = MgO \cdot CaCO_3 + H_2S \ .$$

The carbonated magnesium component of the make-up acceptor is also calcined at these conditions:

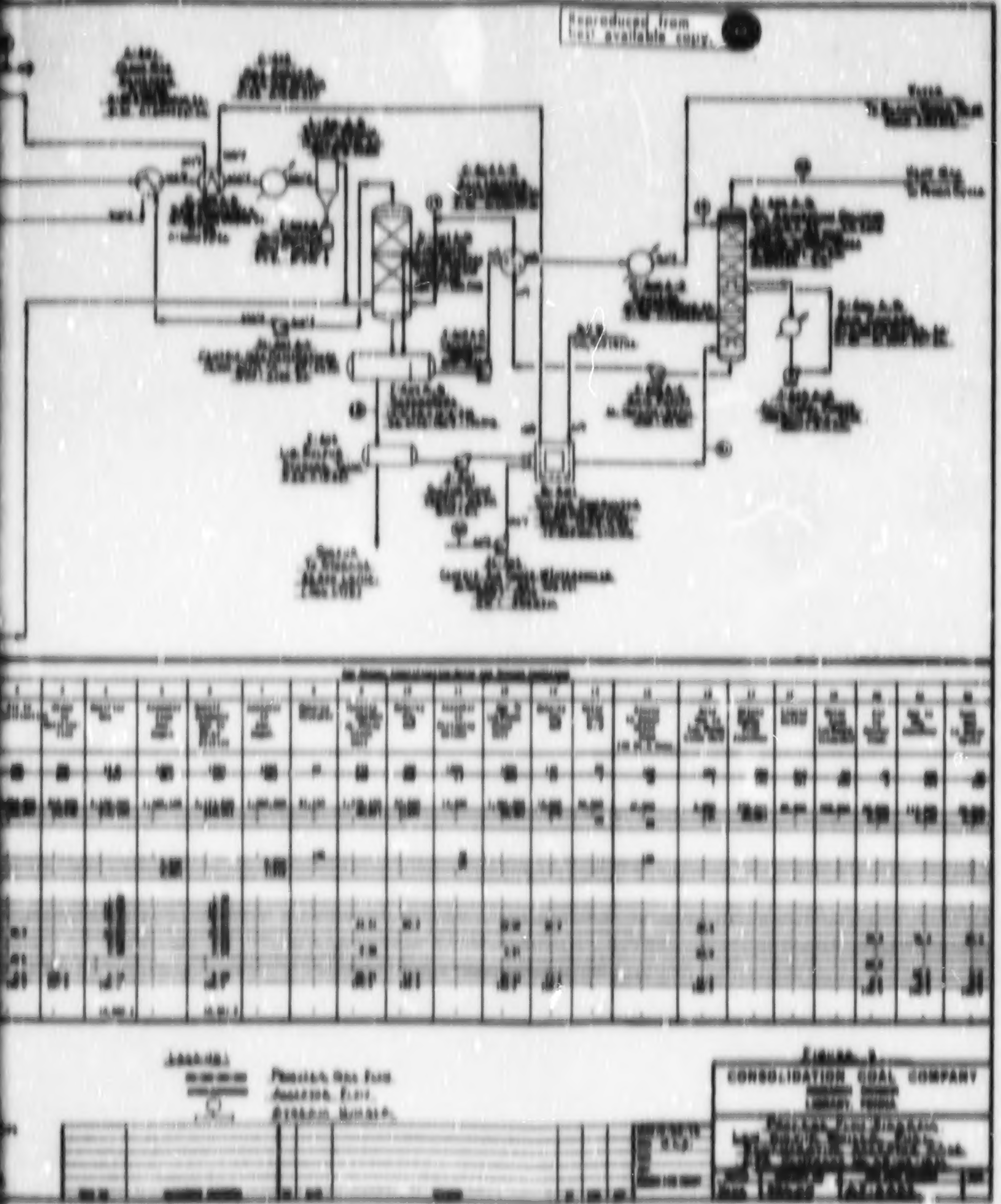
$$MgCO_3 \cdot CaCO_3 = MgO \cdot CaCO_3 + CO_2 \ .$$

The regenerated acceptor is returned to the gas desulfurizer by gravity flow (Stream No. 5). Spent acceptor (1% of the circulating flow) is withdrawn from D-302 via a lockhopper, F-303, and a rotary feeder, L-303 (Stream No. 11). This spent acceptor must be treated before disposal.



Preceding page blank

Reproduced from best available copy.


LEGEND
Process Gas Flow
Process Flow
Stream Number
CONSOLIDATION COAL COMPANY

About 75% of the calcium component of this stream is in the form of CaS. If this were disposed of directly to the station ash pit, H_2S gas would slowly evolve as the CaS was hydrolyzed. To avoid this unacceptable condition, the spent acceptor is directly contacted with CO_2 and water in three stages of stirred reactors, D-303, to convert the CaS to $CaCO_3$. At these conditions, the MgO component of the dolomite would also recarbonate. The overall reaction is,

$$MgO \cdot CaS + 2\ CO_2 + H_2O = MgCO_3 \cdot CaCO_3 + H_2S.$$

The spent acceptor is conveyed hydraulically by a dilute recirculating slurry stream to a hydroclone, G-305. The underflow slurry (controlled at 35 wt.% solids) flows to the three series converters, D-303A, B and C, respectively. Each converter is agitated by a turbine-type mixer, L-305, and some reaction heat is removed in each stage by cooler, C-305. The spent acceptor, stripped of sulfur and fully carbonated, is pumped to the station ash pit by slurry pump, J-301. The overflow slurry from hydroclone, G-305, is continuously recirculated via surge drum, F-304 and circulating pump, J-303. The sensible heat loss from the spent acceptor is removed by cooler, C-304. Make-up water to this system is supplied by station pond overflow via J-302 (which also supplies the water to cool the gasifier ash and convey it to the station ash pond).

Acid gas resulting from the acceptor stripping operation (Stream No. 16), is compressed to system pressure by JC-303 and flows to the liquid-phase Claus reactor.

Sulfur Recovery by Liquid-Phase Claus

The process gas exiting D-302 (Stream No. 15) is passed through two stages of cyclones (G-303 and G-304, respectively), to remove entrained acceptor. The sensible heat content of this stream is then exchanged with recycle gas in exchanger C-401, and with boiler feed water (required for gasification steam) in C-402. An electrostatic precipitator, L-401, is provided to remove all entrained dust. The gas then flows to the bottom of the liquid-phase Claus reactor, D-401.

The concentration of H_2S in the gas from the acceptor regenerator is limited by the equilibrium restriction at 1500°F and amounts to only about 2.6 volume per cent. The liquid-phase Claus reaction developed in this work is uniquely suited to processing this gas. The liquid phase Claus reactor, D-401, operates at 310°F and about 310 psia. Product gas from the acceptor regenerator (Stream No. 15), gas from the reject acceptor stripping section (Stream No. 16), and dilute, aqueous H_2SO_3 (Stream No. 17) are charged to the bottom of the liquid-phase Claus reactor. Flow is upward through a sparged reactor containing only water, as was demonstrated during the experimental work described in the annual report(1) to EPA. Liquid sulfur is produced by the reaction,

$$2\ H_2S + H_2SO_3 = 3\ S + 3\ H_2O.$$

Liquid sulfur and liquid water flow from the reactor to a decanter-type separator, F-402. Unreacted gas (Stream No. 9), saturated with water vapor at 310°F, is compressed by JC-401, reheated in exchanger, C-401 to 975°F and returned to the acceptor regenerator reactor. The sensible heat content of the liquid water from F-402 (Stream No. 18), is exchanged with the feed acid (Stream No. 17) in C-404, further cooled to 90°F in C-405 and charged to the SO_2 absorption tower, D-402.

Approximately one-third of the sulfur from F-402 is burned with stoichiometric air (Stream No. 20) in pressurized combustor, B-401, to produce SO_2. Excess heat is removed to boiler feed water via cooling tubes in the walls. The exit gas from the sulfur combustor (Stream No. 21) flows to the base of the SO_2 absorption tower, D-402. Water (Stream No. 19) flowing down through the packed tower absorbs the SO_2 in the gas by,

$$SO_2 + H_2O = H_2SO_3 \text{ aqueous}$$

Most of the exothermic heat of reaction is removed by side stream cooler, C-406. The vent gas from the absorption tower (Stream No. 22) is at 90°F and 205 psia. It probably would contain some residual SO_2 (assumed in this case as 0.2 volume per cent). The most practical means of disposing of this gas is to bleed it to an intermediate stage of the expansion turbine required for the desulfurized producer gas in the power station. This would decrease the sulfur removal efficiency of this process from 97.0% to 96.5%, but would increase the power output of the station slightly, and would eliminate an entire stack gas scrubbing installation following the SO_2 absorption step.

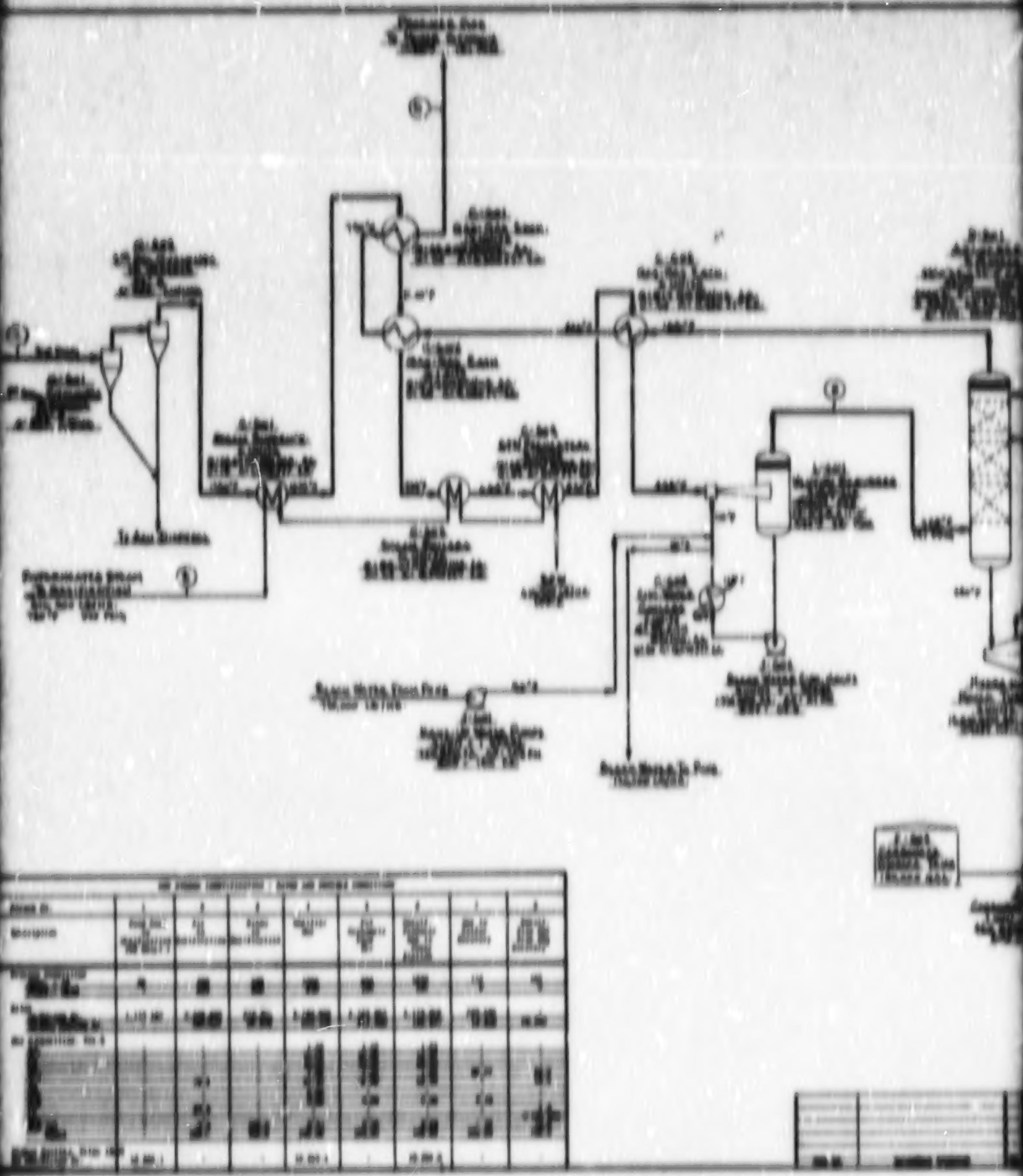
C. Conventional Gas Desulfurization

Sulfur Removal by Hot Potassium Carbonate

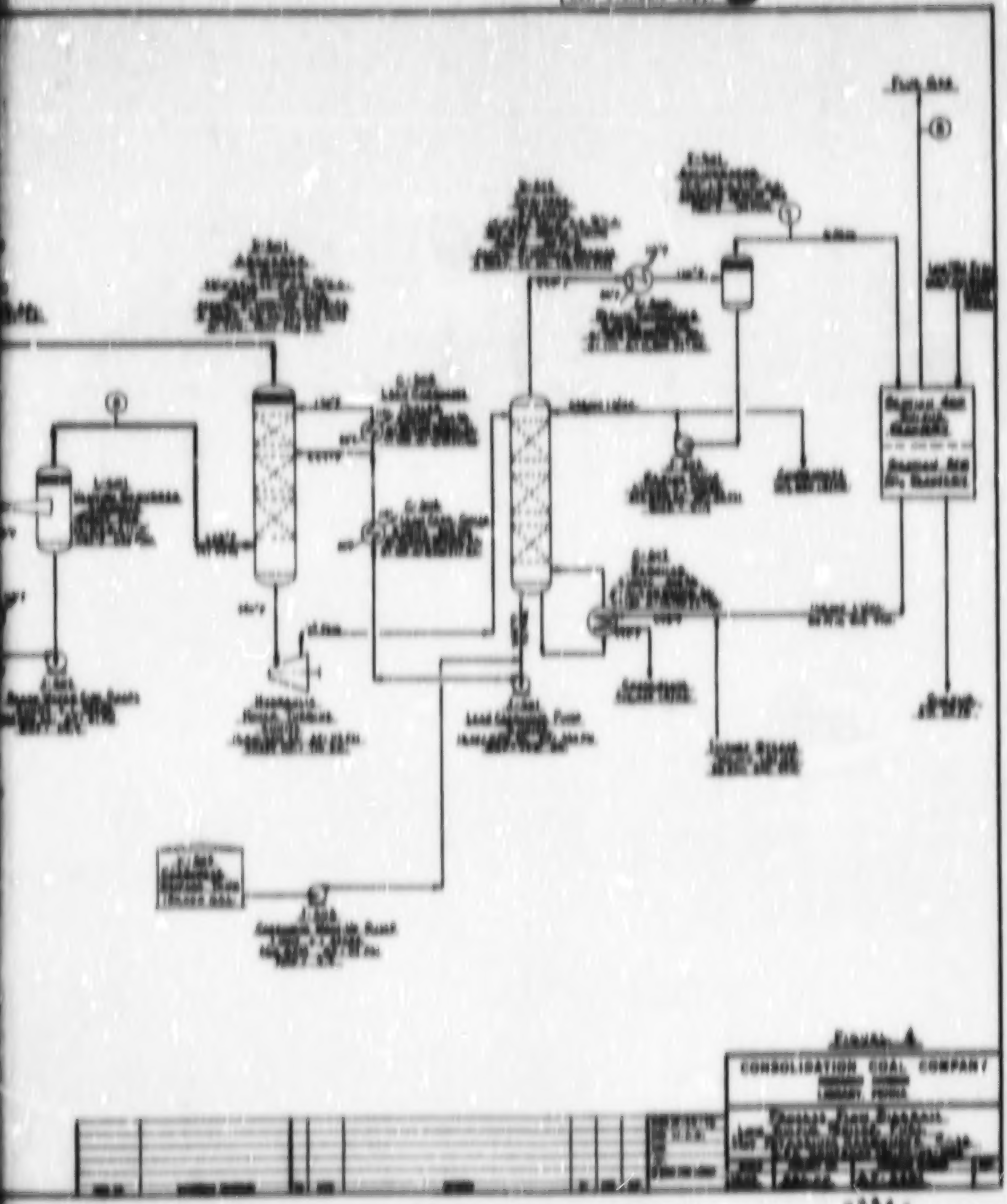
A schematic flow diagram of the proposed commercial embodiment of the conventional gas desulfurization process is shown in Figure 4 (Consol Dwg. AF-3451).

Gasifier product gas (Stream No. 4) at 1750°F and 225 psia passes through two stages of cyclones (G-301 and G-302, respectively), to remove the bulk of the residual dust and is then cooled prior to entering the absorber (D-301). A portion of the sensible heat content of the gas is used to generate and superheat steam required for gasification of the feed coal in heat exchangers C-301, C-302 and C-303, respectively. The remainder of the sensible heat is used to reheat the desulfurized gas leaving the absorber to 1300°F in heat exchangers C-601, C-602 and C-603, respectively.

The gasifier gas, now cooled to 425°F, must be wet scrubbed for particulate and alkali removal prior to contacting the hot carbonate solution. The cooled gas flows to three parallel Venturi scrubbers (L-601) where it is scrubbed by circulating water at the gas dewpoint of 328°F. The circulating water flows to the Venturi scrubbers via the black water pumps, J-602. The



Reproduced from best available copy.


CONSOLIDATION COAL COMPANY
LIBRARY, PENNA
Process Flow Diagram

excess sensible heat in the gas is removed via coolers, C-604, and make-up water enters the system via water pumps, J-601. The make-up water rate is based on an assumed solids loading in the process gas of 5 grains/cubic foot, and a solids content in the circulating water of 2 wt.%. Net solids removed from the gas flow result in a 3 wt.% slurry to the station pond.

Clean gasifier gas (Stream No. 5) at 330°F and 208 psia flows to the bottom of the absorbers (D-301) where the gas is contacted countercurrently in a packed bed with a 25 wt.% solution of hot potassium carbonate. The flow of lean carbonate to the absorbers is split and cooled in the lean carbonate coolers (C-304 and 305) to ensure adequate absorption of H_2S. Most (97.8%) of the H_2S and the bulk (88.0%) of the CO_2 in the gasifier gas is absorbed in the hot carbonate solution, leaving a desulfurized gas with an H_2S content of about 190 ppm by volume. The desulfurized gas exiting the absorbers is then reheated to 1200°F by the aforementioned exchangers (C-601, C-602, and C-603). The desulfurized producer gas at 1200°F and 190 psia (Stream No. 6) is then delivered to the power station. Subsequent use of this gas is dependent on the design of the power station, and is discussed later in this report.

The rich carbonate solution leaving the absorbers is let down to 35 psia by power turbines, which drive in tandem with electric motors the lean carbonate pumps (J-301). The rich carbonate then enters the strippers (D-302) where the pressure is reduced to 27 psia and the solution is stripped with steam. Steam in the stripped acid gas is condensed in water-cooled condensers (C-306) and collected in accumulators (F-301). Some of the condensate is returned to the strippers via reflux pumps (J-302) to maintain water balance and the excess is sent to condensate recovery. The stripped acid gas (Stream No. 7) at 110°F and 21 psia contains about 8% H_2S and is suitable feed to a Claus sulfur recovery unit of the direct oxidation type.

About one-sixth of the reboiler (C-307) low pressure steam requirement is produced by the sulfur recovery and the SO_2 recovery sections. The other five-sixths must be imported.

Make-up carbonate solution is stored in the carbonate storage tank (F-302) and enters the lean carbonate line via the carbonate make-up pump (J-303).

Sulfur Recovery by Direct Oxidation Claus

Acid gas (Stream No. 7) containing about 8% H_2S flows to the sulfur recovery section at 110°F and 21 psia where it is indirectly preheated in a furnace prior to entering the first converter. Oxygen in an air stream reacts directly with H_2S over the converter catalyst to produce SO_2 and sulfur. The hot effluent gas (except bypass for reheating) flows to the first sulfur condenser where sulfur is condensed. The gas leaving the condenser is directly reheated to reaction temperature with about a 15% bypass of converter hot effluent gas. The gas then enters the second converter to obtain equilibrium conversion of H_2S and SO_2 to sulfur and water. The sulfur produced here is condensed in a second sulfur condenser.

Overall sulfur recovery is about 88%. The first plant(8,9) utilizing this process obtained an 89% sulfur recovery from an acid gas feed containing 10% H_2S (dry basis).

The sulfur condensers generate 90,000 lb/hr of low pressure steam (70 psig) while condensing 471 long tons per day of sulfur product.

The tail gas leaving the last condenser passes through a coalescer to remove entrained liquid sulfur and is incinerated at 1000°F. The incinerated tail gas then flows to the SO_2 recovery section. The recovered SO_2 is returned to the converter where it reacts to produce additional sulfur. This gives a net sulfur recovery of 99.8%.

SO_2 Recovery by Wellman-Lord Process

Hot gas from the incinerator is cooled in a waste heat boiler, then quenched and fed to the SO_2 absorber, where SO_2 is absorbed in a lean sodium sulfite solution. The clean gas (Stream No. 8) from the absorber passes to the stack. The concentrated stream of SO_2 recovered from the sodium sulfite solution in the regeneration system is recycled to the sulfur recovery section.

The process net production of low pressure steam is about 70,000 lb/hr.

V. Economic Evaluation

A. General

This evaluation is restricted to the desulfurization of a producer gas from a pressurized coal gasifier for delivery to a conventional gas-burning station at a pressure of 10 psig. Power recovery from the desulfurized producer gas from system pressure (about 300 psig) to 10 psig is best accomplished in an expanding turbine-generator set. The power generated by the turboexpander exceeds the power required for the coal gasifier air compressor. The excess power recovered is a net credit to the process. However, it is beyond the scope of this contract to define the actual dollar value of the power credit.

In hot gas desulfurization, the technical question remains as to the required quality of gas (with respect to content and size of particulate matter and alkali) that may be charged to an expander. The maximum power obviously will be recovered from the turboexpander if the producer gas can be adequately "cleaned" by high pressure drop cyclones alone. Conversely, the gas may be water scrubbed (in conventional venturi scrubbers) and then reheated by indirect heat exchange with hot gas to the scrubbers. This assures the protection of the turboexpander from particle erosion and/or alkali deposition. The penalty is a reduction in power recovery, because gas reheat is only economical to about 1100°F, and an additional pressure loss is incurred through the scrubber and reheat system. There is no incentive to eliminate the venturi scrubber for conventional, low-temperature desulfurization because the gas must be cooled anyway. The Annual Report[1] to EPA covered this technical uncertainty in the hot gas desulfurization process. The process incorporates only the hot particulate removal method for this study.

In both cases, the producer gas after expansion to 10 psig is delivered to the power station as preheated gas (840°F to 880°F). This sensible heat content serves to improve the efficiency (or the heat rate) of the station proper. In a conventional gas-burning station, the fuel gas is delivered at ambient temperature, and sensible heat from the products of combustion is recovered (via combustion air preheat) to an air heater exit temperature of about 300°F. It seems most realistic to credit the process with the excess sensible heat in the preheated producer gas above 300°F as an approximate means of measuring the improvement in the power station efficiency.

B. Plant and Operating Cost Estimates

The capital cost estimate for hot gas desulfurization was developed by the Consol Engineering Department. The estimate for Sections 300 and 400 of Figure 3 is summarized in tabular form in the Appendix as Tables A-1 and A-2. A detailed estimate was not made for Section 500, the make-up CO_2 system, because a conventional "hot pot" unit was assumed. The costs and utility requirements for this type of system are adequately defined in the literature.[10] Similarly the Consol Engineering Department developed a capital cost estimate for conventional desulfurization. The estimate for Sections 300 and 600 of Figure 4 is summarized in the Appendix as Tables B-1 and B-2. For the remaining sections, Section 400, the sulfur recovery system (a direct oxidation Claus unit), and Section 500, the SO_2 recovery system (a Wellman-Lord unit), cost and utility requirements were obtained from the literature.[7,11]

The capital cost estimates developed in the Appendix are defined as inside battery limits (ISBL). To these costs must be added the off-site facilities (OSBL) which include utility costs, electric substations, cooling water towers, distribution piping, and boiler feed water treating. The accuracy of the capital cost estimates in this study is estimated as ± 20%.

It was required in this study to anticipate the escalation in these costs to a presumed start-up date of January, 1978. The economic climate at present defies a logical derivation of these factors. This work is based on these _arbitrary_ assumptions:

1. July, 1973 costs as a base point.
2. Begin design and construction, January, 1974.
3. Begin operation, January, 1978.
4. Escalation at 7½% per year average of construction labor and material.
5. Interest during construction at 7½% simple interest on cash flow.
6. Escalation of direct operating labor at 5½% per year.
7. Interest on working capital at 7½% per year.

The total investment summary for the two cases described above is shown in Table II. The installed plant cost (present day cost) for the hot gas desulfurization scheme (Case I) is $35,800,000, whereas, that for the conventional gas desulfurization scheme (Case II) is $49,800,000. The greater plant cost for the conventional system is mostly associated with wet scrubbing and reheating. Escalation of these costs to January, 1978 (as defined above) increases the total investment to $48,300,000 and $68,800,000, respectively.

Direct operating costs for these two cases were estimated as shown in Table III. Note, that an average plant operating factor of 70% was assumed reflecting power station practice. The unit values used to develop operating costs are shown directly in Table III. The total direct operating cost (January, 1978) for Case II ($10,834,000) is double that of Case I ($5,321,000). This is a result of the large import steam requirement for regeneration of the hot carbonate solution and of the fuel gas requirement for preheat and incineration within the Claus sulfur plant.

C. Evaluation of Desulfurization Cost

The Regenerative Acceptor process based on the results of this economic evaluation has a potential for being substantially cheaper than the conventional liquid absorption processes. Based on the cost estimates presented in Tables II and III, the system costs are estimated as shown in Table IV. The net annual operating costs for Case I (hot regenerative acceptor) are $13,810,000 per year and for Case II (hot potassium carbonate) the costs are $20,416,000 per year. Approximately from one-half to two-thirds of these costs are represented by capital charges. The low value for sulfur credit ($8.00/long ton) reflects a conservative view of the sulfur market.

The make-up acceptor cost has little impact on the hot regenerative acceptor process cost. Since this study does not define a specific plant site, a definitive cost for delivered acceptor cannot be derived. An arbitrary cost of $10.00 per ton of raw stone ($MgCO_3CaCO_3$) was assumed. This somewhat high cost is based on two facts: a) the laboratory studies to date have shown that some dolomitic stones cannot be used in the process (excessive attrition) thereby limiting the potential supply sources, and b) transportation costs for raw materials are substantially increasing. However, even with an acceptor make-up cost of $10.00 per ton, the annual cost is only 4-5% of the total system cost. The imprecision of the acceptor cost has only a minor influence on the evaluation of the total system.

The system costs presented in Table IV are more meaningful if related to either the coal required for the system, or to the quantity and quality of the gas delivered to the power station. The net annual operating costs for Case I are equivalent to $4.03 per ton of feed coal; for Case II, $6.55 per ton. Expressed in terms of heating value of the coal, the corresponding costs are 16.9 and 27.4¢/MM Btu, respectively.

[illegible]

[illegible]

[illegible]	[illegible]				[illegible]				
[illegible]	[illegible]				[illegible]				
[illegible]	[illegible]				[illegible]				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]									
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]									
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]								
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]									
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]				[illegible]					[illegible]
[illegible]				[illegible]					[illegible]
[illegible]				[illegible]					[illegible]
[illegible]				[illegible]					[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
7. [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
8. [illegible]										
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]				[illegible]						[illegible]
[illegible]				[illegible]						[illegible]

[illegible]

[illegible]

Table IV

Economic Evaluation
Hot vs Conventional Desulfurization Process

Basis: [illegible] Plant Operating Factor ([illegible] hr/yr)

Case	I	II
Method of Gas Desulfurization	Hot	Conventional
Desulfurization Process	Regenerative Acceptor	Hot Potassium Carbonate
Coal Required:		
Tons/yr (10% Moisture)	[illegible]	
Higher Heating Value, Btu/yr	[illegible]	
Desulfurized Producer Gas to Station		
Mols/Hr	[illegible]	[illegible]
Temperature	[illegible]°F	[illegible]°F
Pressure	10 psig	10 psig
Higher Heating Value, Btu/yr	[illegible]	[illegible]
HHV + Sensible Heat Content, Btu/yr(1)	[illegible]	[illegible]
Cost Analysis		
Installed Plant Cost (1973)	$[illegible] MM	$[illegible] MM
Escalation to 1978	[illegible] MM	[illegible] MM
Interest during Construction	[illegible] MM	[illegible] MM
Total Investment	$[illegible] MM	$[illegible] MM
Working Capital	$ [illegible] MM	$ [illegible] MM
Annual Operating Costs		
Direct Operating Cost (1978 Basis)	$ [illegible] MM/Year	$[illegible] MM/Year
Acceptor at $[illegible]/ton	[illegible] MM/Year	0 MM/Year
Interest on Working Capital at 7.5%	[illegible] MM/Year	[illegible] MM/Year
Capital Charges at [illegible]% Investment	[illegible] MM/Year	[illegible] MM/Year
Sulfur Credit at $[illegible]/metric ton	($ [illegible] MM/Year)	($ [illegible] MM/Year)
Net Annual Operating Cost	$[illegible] MM/Year	$[illegible] MM/Year
Desulfurization Cost Expressed:		
In terms of feed coal		
$/ton coal	[illegible]	[illegible]
¢/MM Btu HHV	[illegible]	[illegible]
In terms of product gas to station:		
¢/MM Btu HHV	[illegible]	[illegible]
¢/MM Btu (HHV + Sens. Ht.)(1)	[illegible]	[illegible]
Excess Power Generated by Expander	[illegible] MW	[illegible] MW

(1) Sensible heat content above an assumed air heater outlet temp. of [illegible]°F.

[illegible]

Considering only the higher heating value of the product gas to the power station, the corresponding costs are 31.6 and 34.7¢/MM Btu for Cases I and II, respectively. Allowing for the sensible heat credit discussed earlier, the costs are reduced to 30.1 and 33.9¢/MM Btu, respectively. Note, that the sensible heat credit reduces the process cost by about 4-5%. Wet scrubbing and gas reheat increases the processing cost of Case II by 6.3¢/MM Btu or 24%.

As discussed earlier, another credit to the process is the excess power generated by the expanding turbine-generator set. For Case I this amounts to 180 MW; for Case II, 100 MW. As noted previously, it is beyond the scope of this contract to evaluate the dollar credit associated with this excess power. Consequently, the cost of the expanding turbine-generator set is not included in the investment cost. However, the impact of the credit upon the processing costs can be at least qualitatively defined. The real cost of electric power generated by an expanding turbine-generator set would normally be less than steam-generated power. If the real cost was one mill/KWH less, then the credit to the process would be for Case I, 1.6¢/MM Btu, and for Case II, 1.1¢/MM Btu. These are significant credits, but could only be evaluated with accuracy through a detailed study.

G. D. Rutledge

G. D. Rutledge

J. T. Clancey

J. T. Clancey

GDR/JTC:mm

Attachments: Bibliography
Appendix A
Appendix B

Bibliography

1. Curran, G. P., et al, "Development of the CO_2 Acceptor Process Directed Towards Low-Sulfur Boiler Fuel," Annual Report to Control Systems Division Office of Research and Monitoring Environmental Protection Agency under Contract No. EHSD 71-15, March 15, 1972-June 30, 1973. (Not yet published.)

2. Benson, H. E. and J. H. Field, Petroleum Refiner, 39, 127, April, 1960.

3. Bonard, J. P. and B. J. Mayland, Hydrocarbon Processing and Petroleum Refiner, 41, 158, April, 1962.

4. Buck, R. G. and Angus R. B. Leitch, Petroleum Refiner, 37, 241, November, 1958.

5. Goolsbee, J. A. and H. E. McLaughlin, Petroleum Refiner, 39, 189, January, 1960.

6. Garrett, E. Peck, the Oil and Gas Journal, p. 76, December 15, 1969.

7. Hydrocarbon Processing (NG/LNG/SNG Handbook) 52, 116, April 1973.

8. Grekel, H. et al, Chemical Engineering Progress, 61, 70, September, 1965.

9. Chemical Engineering, p. 38, April 1, 1974.

10. Katell, Sidney and John H. Faber, Petroleum Refiner, 39, 187, March, 1960.

11. Grekel, H. et al., the Oil and Gas Journal, p. 88, October 28, 1968.

Appendix A

Detailed Investment Costs for Hot Gas Desulfurisation

[illegible]

[illegible]

Appendix B

Detailed Investment Costs for Conventional Gas Desulfurization

[illegible]

[illegible]

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–					[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]
			[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		[illegible]		[illegible]	–					
	[illegible]		[illegible]		[illegible]	[illegible]					[illegible]
	[illegible]		[illegible]		[illegible]	[illegible]				[illegible]	
	[illegible]		[illegible]		[illegible]	[illegible]			[illegible]		
	[illegible]		[illegible]		[illegible]	[illegible]		[illegible]			
	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]				
	[illegible]		[illegible]		[illegible]	[illegible]					
	[illegible]		[illegible]		[illegible]	[illegible]					
			[illegible]		[illegible]	[illegible]					
			[illegible]		[illegible]						
[illegible]			[illegible]		[illegible]						
			[illegible]		[illegible]						

[illegible]

TABLE [illegible]

[illegible]

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Major	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					[illegible]
			Total Major Equipment		[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]
Minor	[illegible]		[illegible]		[illegible]	-					[illegible]
	[illegible]		[illegible]		[illegible]	[illegible]				[illegible]	
	[illegible]		[illegible]		[illegible]	[illegible]			[illegible]		
	[illegible]		[illegible]		[illegible]	[illegible]		[illegible]			
	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]				
	[illegible]		[illegible]		[illegible]	[illegible]					
	[illegible]		[illegible]		[illegible]	[illegible]					
	[illegible]		[illegible]		[illegible]	[illegible]					
			Total Minor Equipment		[illegible]	[illegible]					
			Total E + L =		[illegible]						
Indirect	[illegible]		[illegible]		[illegible]						
			Total Investment =		[illegible]						

[illegible]

APPENDIX B

Conversion Factors - English to Metric Units

	English System	Metric Equivalent
Length	inch foot	2.54 centimeter 0.305 meter
Area	square foot	0.093 square meter
Volume	gallon cubic foot	3.785 liter 28.32 liters
Mass	pound	453.6 grams
Pressure	pound per square inch atmosphere atmosphere	51.70 millimeters Hg 760 millimeters Hg 101.3 kilopascals
Temperature	° Fahrenheit	1.8 (° Celsius) + 32
Energy	Btu horsepower hour	1055 joules 2.68 x 10^6 joules